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TREATMENT OF CONTAMINATED SOILS WITH AQUEOUS SURFACTANTS

by

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Contract No. 68-03-3113

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16. ABSTRACT

The overall objective of this project was to develop a technical base for decisions on the use of chemical countermeasures at releases of hazardous substances. Work included a literature search to determine the nature and quantities of contaminants at Superfund sites and the applicability of existing technology to in situ treatment of contaminated soils. Laboratory studies were conducted to develop an improved in situ treatment methodology and were designed to determine whether significant enhancement to the efficiency of water washing could be obtained by adding aqueous surfactants to recharge water used in a continuous recycle.

The use of aqueous nonionic surfactants for cleaning soil spiked with PCBs, petroleum hydrocarbons, and chlorophenol was developed through shaker table and soil column tests. Contaminant removal from the soil was 92% for the PCBs, using 0.75% each of Adsee 799® (Witco Chemical) and Hyonic NP-90® (Diamond Shamrock) in water. For the petroleum hydrocarbons, the removal with a 2% aqueous solution of each surfactant was 93%. These removals are orders of magnitude greater than obtained with just water washing and represent a significant improvement over existing in situ technology.

Treatability studies of the contaminated leachate were also performed to investigate separating the surfactant from the contaminated leachate to allow reuse of the surfactant. A method for separating the surfactant plus the contaminant from the leachate was developed; however, all attempts at removing the surfactant alone proved unsuccessful.

Based upon project results, the aqueous surfactant countermeasure is potentially useful for in situ cleanup of hydrophobic and slightly hydrophilic organic contaminants in soil, and should be further developed on a larger scale at a small contaminated site under carefully controlled conditions. However, reuse of the surfactant is essential for cost-effective field application. Accordingly, any future work should investigate the use of other surfactants that may be more amenable to separation.

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FOREWORD

Today's rapidly developing and changing technologies and industrial products and practices frequently carry with them the increased generation of solid and hazardous wastes. These materials, if improperly dealt with, can threaten both public health and the environment. Abandoned waste sites and accidental releases of toxic and hazardous substances to the environment also have important environmental and public health implications. The Hazardous Waste Engineering Research Laboratory assists in providing an authoritative and defensible engineering basis for assessing and solving these problems. Its products support the policies, programs, and regulations of the Environmental Protection Agency, the permitting and other responsibilities of State and local governments and the needs of both large and small businesses in handling their wastes responsibly and economically.

This report describes the development of a countermeasure for *in situ* cleanup of organic soil contaminants using aqueous surfactants, and will be useful to those who develop and test *in situ* chemical countermeasures. For further information, please contact the Land Pollution Control Division of the Hazardous Waste Engineering Research Laboratory.

David G. Stephan, Director
Hazardous Waste Engineering
Research Laboratory

ABSTRACT

This report presents the results, conclusions, and recommendations of a project performed to develop a technical base for decisions on the use of chemical countermeasures at releases of hazardous substances. The project included a brief literature search to determine the nature and quantities of contaminants at Superfund sites and the applicability of existing technology to in situ treatment of contaminated soils. Laboratory studies were conducted to develop an improved methodology applicable to the in situ treatment of organic chemical contaminated soil.

Current technology for removing contaminants from large volumes of soils (too large to excavate economically) has been limited to in situ "water washing." Accordingly, the laboratory studies were designed to determine whether the efficiency of washing could be enhanced significantly (compared to water alone) by adding aqueous surfactants to the recharge water and recycling them continuously.

The use of an aqueous nonionic surfactant pair for cleaning soil spiked with PCBs, petroleum hydrocarbons, and chlorophenols was developed through bench scale shaker table tests and larger scale soil column tests. The extent of contaminant removal from the soil was 92 percent for the PCBs, using 0.75 percent each of Adsee 799® (Witco Chemical) and Hyonic NP-90® (Diamond Shamrock) in water. For the petroleum hydrocarbons, the removal with a 2 percent aqueous solution of each surfactant was 93 percent. These removals are orders of magnitude greater than obtained with just water washing and represent a significant improvement over existing in situ cleanup technology.

Treatability studies of the contaminated leachate were also performed to investigate separating the surfactant from the contaminated leachate to allow reuse of the surfactant. A method for separating the surfactant plus the contaminant from the leachate was developed; however, all attempts at removing the surfactant alone proved unsuccessful.

Based upon the results of the laboratory work, the aqueous surfactant countermeasure is potentially useful for in situ cleanup of hydrophobic and slightly hydrophilic organic contaminants in soil, and should be further developed on a larger scale at a small contaminated site under carefully controlled conditions. However, reuse of the surfactant is essential for cost-effective application of this technology in the field. Accordingly, any future work should investigate the use of other surfactants/surfactant combinations that may be more amenable to separation.

This report was submitted in partial fulfillment of Contract No. 68-03-3113 by SAIC/JRB Associates under the sponsorship of the U.S. Environmental Protection Agency. This report covers the period from May 1982 to August 1985, and work was completed on August 23, 1985.

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ABBREVIATIONS AND SYMBOLS

CEC	-- cation exchange capacity
cm	-- centimeter
cm/sec	-- centimeters per second
cm^2	-- square centimeters
DI	-- deionized
ECD	-- electron capture detector
EOR	-- enhanced oil recovery
EPG	-- Emulsan Purified Grade from Petroferm
ETG	-- Emulsan Technical Grade from Petroferm
FID	-- flame ionization detector
ft	-- feet
g	-- gram
g/cm^3	-- grams per cubic centimeter
g/g	-- grams per gram
GC	-- gas chromatography
GC/MS	-- gas chromatography/mass spectrometry
HCB	-- hexachlorobenzene
HPLC	-- high performance liquid chromatography
hr	-- hour
in	-- inch
kg	-- kilogram
l	-- liter
LC	-- liquid chromatography
lb	-- pound
lb/ft^3	-- pounds per cubic foot
log P	-- log (base 10) of octanol/water partition coefficient
m	-- meter
mg	-- milligram
mg/l	-- milligrams per liter
ml	-- milliliter
mm	-- millimeter
m^3/s	-- cubic meters per second
NaPEG	-- sodium polyethylene glycolate
ng	-- nanogram
nm	-- nanometer
PBB	-- polybrominated biphenyl
PCB	-- polychlorinated biphenyl
pcf	-- pounds per cubic foot
POTW	-- publicly owned treatment works
ppb	-- parts per billion
ppm	-- parts per million
PVA	-- polyvinyl alcohol
rpm	-- revolutions per minute
TOC	-- total organic carbon
UV-VIS	-- Ultraviolet-Visible
ug	-- microgram
ug/ml	-- microgram per milliliter
um	-- micrometer
ul	-- microliter

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This document was prepared by SAIC/JRB Associates for EPA's Office of Research and Development in partial fulfillment of Contract No. 68-03-3113, Task 29-1. Mr. Anthony N. Tafuri of the Hazardous Waste Engineering Research Laboratory, Releases Control Branch, Edison, New Jersey, was the Project Officer. The work presented in this document was performed by Dr. William D. Ellis, Dr. James R. Payne, Mr. G. Daniel McNabb, and Mr. James Lambach of Science Applications International Corporation (SAIC), with the assistance of Messrs. Daniel Baxter, Michael Beckel, Nicholas DeSalvo, Ms. Dana Errett, Messrs. Gary Farmer, Michael Guttman, Joseph Rotola, and Nicholas Trentacoste, all of SAIC, and Mr. James Nash of Mason and Hanger - Silas Mason Company, Inc.

SECTION 1

INTRODUCTION

The "Comprehensive Environmental Response, Compensation, and Liability Act of 1980" (CERCLA or Superfund) recognizes the need to develop countermeasures (mechanical devices, and other physical, chemical, and biological agents) to mitigate the effects of hazardous substances that are released into the environment and are needed to clean up inactive hazardous waste disposal sites. One key countermeasure is the use of chemicals and other additives that are intentionally introduced into the environment for the purpose of controlling the hazardous substance. The indiscriminate use of such agents, however, poses a distinct possibility that the release situation could be made worse by the application of an additional chemical or other additive.

The U.S. Environmental Protection Agency's Hazardous Waste Engineering Research Laboratory has initiated a Chemical Countermeasures Program to define technical criteria for the use of chemicals and other additives at release situations of hazardous substances such that the combination of the released substance plus the chemical or other additive, including any resulting reaction or change, results in the least overall harm to human health and to the environment.

The Chemical Countermeasure Program has been designed to evaluate the efficacy of in situ treatment of large volumes of subsurface soils, such as found around uncontrolled hazardous waste sites, and treatment of large, relatively quiescent waterbodies contaminated with spills of water-soluble hazardous substances. For each situation, the following activities are planned: a literature search to develop the body of existing theory and data; laboratory studies on candidate chemicals to assess adherence to theory and define likely candidates for full-scale testing; full-scale, controlled-condition, reproducible tests to assess field operation possibilities; and full-scale tests at a site requiring cleanup (i.e., a "site of opportunity").

This project, to develop the use of aqueous surfactants for in situ washing of soils contaminated with hydrophobic (water insoluble) organics and slightly hydrophilic (slightly water soluble) organics, was the first technique to be developed under the Chemical Countermeasures Program. Another countermeasure for soils, the use of acids and chelating agents for washing heavy metals from soils, is also being developed under the Program.

The Aqueous Surfactant Countermeasures Project included an information search and laboratory development of the countermeasures. The results and conclusions from the information search formed the basis for the laboratory

development work. Similarly, the results and conclusions from the laboratory work are intended to provide the basis for another project involving large-scale testing of a chemical countermeasure, either in a large test tank (e.g., 15 m x 15 m x 7.5 m deep), or under controlled conditions at a similarly sized contaminated site or portion of a site of opportunity.

SECTION 2

INFORMATION SEARCH

The information search was conducted to determine the nature and quantities of hazardous soil contaminants at Superfund sites, and to assess the applicability of existing technology to in situ treatment of contaminated soils. To determine what types of soil contaminants requiring cleanup were likely to be found at hazardous waste sites, a survey was made of the contaminants at 114 high priority Superfund sites. The classes of chemical wastes found at the most sites were, in order of decreasing prevalence:

- Slightly water soluble organics (e.g., aromatic and halogenated hydrocarbon solvents, chlorophenols)
- Heavy metal compounds
- Hydrophobic organics (e.g., PCBs, aliphatic hydrocarbons).

The survey results are presented in Table 1. A variety of chemical treatment methods were considered that might prove effective in cleaning up soils contaminated with these wastes. However, methods for in situ chemical treatment of soils will probably be feasible and practical for only certain cleanup problems. They can be expected to be potentially most effective for cleanups under the following conditions:

- The contamination is spread over a relatively large volume of subsurface soil, e.g., 100 to 100,000 m^3, at a depth of 1 to 10 m
- The contamination is not highly concentrated, e.g., not over 10,000 ppm total, or the highly concentrated portion of the site has been removed or sealed off
- The contaminants can be dissolved or suspended in water, degraded to nontoxic products, or rendered immobile, using chemicals that can be carried in water to the zones of contamination.

For contamination less than 1 m deep, other methods such as landfarming (surface tilling to promote aerobic microbial degradation of organics) would probably be more practical. For highly contaminated zones of an uncontrolled hazardous waste landfill or a spill site, methods such as excavation and removal, or excavation and onsite treatment would probably be more practical than in situ cleaning of the soil.

It was recognized that the use of aqueous surfactant solutions, which had

TABLE 1. HAZARDOUS SOIL CONTAMINANTS AT SUPERFUND SITES

	Number of Sites	Total Site Score	Examples
Slightly Hydrophilic Organics		76	
Aromatics			
Benzene	9		
Toluene	8		
Xylene	5		
Other aromatics	3		styrene, naphthalene
Halogenated hydrocarbons			
Trichloroethylene	11		
Ethylene dichloride	6		
Vinyl chloride	4		
Methylene chloride	3		
Other halogenated hydrocarbons	15		chloroform, trichloro ethane, tetrachloro-ethylene, trichloro-fluoromethane
Phenols	12		picric acid, pentachloro-phenol, creosote
Heavy Metal Wastes		47	
Chromium	9		
Arsenic	8		
Lead	7		
Zinc	5		
Cadmium	4		
Iron	3		
Copper	2		
Mercury	2		
Selenium	2		
Nickel	1		
Vanadium	1		
Fly ash	1		
Plating wastes	2		

(continued)

TABLE 1. HAZARDOUS SOIL CONTAMINANTS AT SUPERFUND SITES (Continued)

	Number of Sites	Total Site Score	Examples
Hydrophobic Organics		38	
Polychlorinated biphenyls	15		
Oil, grease	11		
Volatile hydrocarbons	6		Varsol, hexane
Chlorinated hydrocarbon pesticides	5		endrin, lindane, DDT, 2,4,5-T, dieldrin
Polynuclear aromatics	1		
Other Inorganics		26	
Cyanides	6		
Acids	7		sulfuric acid
Alkalis	6		lime, ammonia
Radioactive wastes	3		uranium mining and purification wastes, radium, tritium
Miscellaneous	4		beryllium, boron hydride, sulfides, asbestos
Hydrophilic Organics		8	
Alcohols	4		methyl, isopropyl, butyl
Other hydrophilics	4		dioxane, bis(2-chloroethyl) ether, urethane, rocket fuel
Unspecified Organic Solvents and Other Organics		30	dioxin, dioxane, dyes, pigments, inks, paints, nitrobenzene

been shown in laboratory tests to flush spilled gasoline from sand (Texas Research Institute (TRI), 1979), might be used for in situ washing of slightly hydrophilic (water soluble) and hydrophobic organics from soils. TRI used a combination of equal parts of Witco Chemical's Richonate®-YLA, an anionic surfactant, and Diamond Shamrock's Hyonic® NP-90, a nonionic surfactant.

To further verify which organic waste chemicals should be targeted for countermeasures development, Field Investigation Team (FIT) summaries were examined for the approximate order of magnitude of the maximum concentrations of organic contaminants in the soil and groundwater surrounding 50 Superfund sites. The FIT Summaries provided data on the concentrations of the following numbers of soil contaminants:

- 17 hydrophobic (water insoluble) organics
- 7 slightly hydrophilic (water soluble) organics
- 12 heavy/toxic metals
- 1 toxic inorganic anion.

No soil concentrations of hydrophilic organics were found. The categories of organic compounds were based on the logarithm of the octanol/water partition coefficients (log P) of the compounds, as follows:

- Hydrophobic organics: $\log P > 3.00$
- Slightly hydrophilic organics: $1.00 < \log P \leq 3.00$
- Hydrophilic organics: $\log P < 1.00$.

The log P is an approximate measure of the tendency of a compound to adsorb to soil rather than dissolve in water. Many hydrophobics, but no hydrophilics, were detected in the soils, because hydrophilics tend to be washed from soil by infiltrating rainwater. Hydrophobics had the highest levels of all the organic contaminants, with 11 compounds averaging in the 1 to 100 ppm range, and with chlordane exceeding 1,000 ppm at one site. The soil concentrations of slightly hydrophilic compounds were in the range of 0.001 to 10 ppm; only two of the seven slightly hydrophilic compounds found, xylene and phenol, were 1 ppm or above. Additional slightly hydrophilic organics were found in the groundwater, because they also tend to be washed from soil. The FIT Summary maximum concentration data are presented in Tables 2, 3, and 4.

Based on these findings, two hydrophobic and one slightly hydrophilic pollutant groups were chosen as model contaminants for testing and development of an aqueous surfactant countermeasure:

- High boiling Murban crude oil fraction containing aliphatic and aromatic hydrocarbons
- PCB mixture in chlorobenzenes (Aroclor® 1260 transformer oil)
- Di-, tri-, and pentachlorophenols mixture.

A representative soil was chosen, based on a study of the characteristics of soils at ten Superfund sites in EPA Region II. The countermeasure was laboratory-tested on the soil spiked with each of the three contaminant groups.

TABLE 2. MAXIMUM CONCENTRATIONS OF HYDROPHOBIC ORGANICS AT 50 SUPERFUND SITES[a]

	SOIL NEAR SITES		GROUNDWATER	
	MAXIMUM CONCEN-TRATIONS[b] (ppm)	NUMBER OF SITES WHERE DETECTED	MAXIMUM CONCEN-TRATIONS[b] (ppm)	NUMBER OF SITES WHERE DETECTED
Chlordane	1,000-10,000	1	-	-
Dieldrin	10-100	1	-	-
Anthracene	10-100	1	-	-
Benzo(a)anthracene	10-100	1	c	1
Benzo(a)pyrene	10-100	1	c	1
Fluoranthene	10-100	1	-	-
Pyrene	10-100	1	-	-
DDT	10-100	2	-	-
Bis(2-ethylhexyl) Phthalate	1-100	3	0.1-10	2
Di-n-butyl Phthalate	1-10	1	-	-
o-Dichlorobenzene	1-10	2	c	1
PCBs	0.1-10	7	10-100	2
Dioxin	0.1-1	1	-	-
Naphthalene	c	1	100-1,000	3
Oil	c	1	1-10	4
Grease	c	1	-	-
1,2,4-Trichlorobenzene	c	1	-	-
Hexachlorobutadiene	-	-	10-100	1
Ethyl Benzene	-	-	1-1,000	4
Bis(2-ethylhexyl) Adipate	-	-	1-10	1
Cyclohexane	-	-	c	1
Benzo(b)pyrene	-	-	c	1
1,1,2-Trichlorotrifluoroethane	-	-	c	1

(a) "Hydrophobic" means log P > 3.00 (P = octanol/water partition coefficient).
(b) Order of magnitude ranges of the highest levels found at a site.
(c) Detected; concentration not reported.

TABLE 3. MAXIMUM CONCENTRATIONS OF SLIGHTLY HYDROPHILIC ORGANICS AT 50 SUPERFUND SITES[a]

	SOIL NEAR SITES		GROUNDWATER	
	MAXIMUM CONCEN-TRATIONS[b] (ppm)	NUMBER OF SITES WHERE DETECTED	MAXIMUM CONCEN-TRATIONS[b] (ppm)	NUMBER OF SITES WHERE DETECTED
Xylene	1-10	1	0.1-100	4
Phenol	1-10	4	0.01-0.1	3
Perchloroethylene	c	1	0.1-100	5
Methylene Chloride	c	1	0.01-100	6
Toluene	c	3	0.01-100	9
Trichloroethylene	c	2	0.001-100	10
Carbon Tetrachloride	c	1	0.1-1	
Dichlorophenol	-	-	10-100	1
Vinylidene Chloride	-	-	10-100	4
Methyl Chloroform	-	-	0.001-100	4
Chloroform	-	-	0.001-100	8
Ethyl Chloride	-	-	1-10	1
Fluorotrichloromethane	-	-	1-10	
Methyl Isobutyl Ketone	-	-	1-10	
Vinyl Chloride	-	-	0.1-10	4
Ethylene Dichloride	-	-	0.01-10	4
1,2-Dichloroethylene	-	-	0.01-10	
Benzene	-	-	0.001-10	9
1,2-Diphenylhydrazine	-	-	0.1-1	
Tetrahydropyran	-	-	0.1-1	1
1,1-Dichloroethane	-	-	0.01-1	4
Chlorobenzene	-	-	0.01-0.1	3
2-Ethyl-4-methyl-1,3-dioxolane	-	-	c	1
Isopropyl Ether	-	-	c	1

(a) "Slightly hydrophilic" means $1.00 < \log P < 3.00$ (P = octanol/water partition coefficient).
(b) Order of magnitude ranges of the highest levels found at a site.
(c) Detected; concentration not reported.

TABLE 4. MAXIMUM CONCENTRATIONS OF HYDROPHILIC ORGANICS AT 50 SUPERFUND SITES[a]

	SOIL NEAR SITES		GROUNDWATER	
	MAXIMUM CONCEN-TRATIONS[b] (ppm)	NUMBER OF SITES WHERE DETECTED	MAXIMUM CONCEN-TRATIONS[b] (ppm)	NUMBER OF SITES WHERE DETECTED
Acetone	-	-	0.01-10,000	4
Methyl Ethyl Ketone	-	-	1-10	3
Acrolein	-	-	0.1-1	1
Tetrahydrofuran	-	-	0.1-1	2
1,4-Dioxane	-	-	0.01-0.1	1
Acrylonitrile	-	-	c	1
Isobutanol	-	-	c	1
2-Propanol	-	-	c	1

(a) "Hydrophilic" means log P < 1.00 (P = octanol/water partition coefficient).
(b) Order of magnitude ranges of the highest levels found at a site.
(c) Detected; concentration not reported.

2.1 POTENTIAL IN SITU CHEMICAL COUNTERMEASURES FOR SOILS

The results of this information gathering on soil countermeasures are shown in Table 5. The table lists the four categories of hazardous waste materials previously identified as significant, several potential in situ mitigation techniques for each hazardous waste category, and key citations to the sources of information.

2.1.1 Hydrophobic Organics

The in situ treatment of hydrophobic organics can sometimes be accomplished by water injection/recovery systems using additives, followed by final treatment above ground. In general, effectiveness of these treatment

TABLE 5. POTENTIAL IN SITU CHEMICAL COUNTERMEASURES FOR SOILS

Hazardous Waste	In Situ Treatment	Selected References
Slightly hydrophilic organics	• Water injection/recovery system with surfactants	Texas Research Institute (1979, 1982b)
	• Chemical and aerobic oxidation	Dragun and Helling (1982) Texas Research Institute (1982a)
Heavy metal wastes	• Sulfide precipitation	Pohland et al. (1981, 1982) USEPA (1979) Huibregtse and Kastman (1978)
	• Fixation with municipal refuse	Myers et al. (1980) Phung et al. (1982) Kinman et al. (1982) Jones and Malone (1982)
	• Water leaching to dissolve and/or flush with injection/recovery system	Epstein et al. (1978) Fuller and Korte (1976) Huibregtse et al. (1978)
Hydrophobic organics	• Water injection/recovery system with:	
	Surfactants	Hill et al. (1973)
	NaOCl, H_2O_2 reactions	Chou et al. (1982)
	Micellar-polymer, e.g., petroleum sulfonates - polyacrylamides	Klins et al. (1976)

(Continued)

TABLE 5. (Continued)

Hazardous Waste	In Situ Treatment	Selected References
Hydrophobic organics (continued)	Solvents	Anderson et al. (1982) Griffin and Chou (1980)
	• Sodium polyethylene glycol reactant	Pytlewski et al. (1980)
Hydrophilic organics	• Water injection/recovery system with:	
	pH adjustment (buffering)	Laguros and Robertson (1978)
	Surfactants	Hill et al. (1973) Texas Research Institute (1979, 1982b)
	NaOCl, H_2O_2 reactions	Chou et al. (1982)
	Micellar-polymer, e.g., petroleum sulfonates - polyacrylamides	Klins et al. (1976)

techniques is limited by the strong soil adsorption of hydrophobic organics (Chou et al., 1981; Griffin and Chou, 1980). Therefore, any successful recovery technique must first desorb the organic from the soil, either by dissolving it in an appropriate micellar emulsion, dissolving it in a good organic solvent, or destroying the soil's sorption capacity in order to flush the hydrophobic contaminant to recovery.

A significant range of chemical additives, polymers, and surfactants has been proposed to overcome the soil/organic adsorbence and flush hydrophobic organics from contaminated soil at hazardous waste sites.

Law Engineering Testing Company (1982) completed an inventory of treatment techniques applicable to gasoline-contaminated groundwater for the American Petroleum Institute and proposed a number of treatment options for further study. Texas Research Institute (1979) completed several laboratory column and two-dimensional modeling studies on the use of surfactants to enhance gasoline recovery from sand. The results showed that a combination of commercial nonionic (Hyonic® PE-90) and anionic (Richonate®-YLA) surfactants was effective in displacing gasoline from the column sand packs. Up to 40 percent of the residual gasoline after initial flooding was removed from the sand using this surfactant combination.

Subsequently, Texas Research Institute (1982b) completed a study on surfactant-enhanced gasoline recovery in a large-scale model aquifer. Three surfactant application procedures were tested: a single application percolated down through the sand bed, multiple applications by percolation, and daily application into the water table. The percentages of gasoline removed associated with each procedure were 6, 76, and 83, respectively.

Texas Research Institute (1982a) also conducted studies on the microbial degradation of underground gasoline by increasing available oxygen. The Institute has also initiated research on the use of hydrogen peroxide to provide oxygen for underground degradation of gasoline (C. Carlson, API, personal communication, April 1982).

Griffin and Chou (1980) demonstrated that polybrominated biphenyls (PBBs), which are similar in behavior to polychlorinated biphenyls (PCBs), and hexachlorobenzene (HCB) are highly resistant to aqueous phase mobility through earth materials. They are highly mobile in organic solvents such as dioxane, and to a lesser extent in pure acetone and methanol. The solubility of these materials in water can be directly correlated with dissolved organics in the waters. Recent studies by Anderson et al. (1982) on the effect of organic fluids on permeability of clay soil liners confirmed the significant impact of acetone and methanol on clay soils. Acetone increased permeability, probably as a result of soil dehydration, while methanol increased permeability perhaps as a result of a decrease in interlayer spacing and accompanying structural changes. The use of these solvents appears promising as a means to recover hazardous organics from uncontrolled releases, but treatment above ground and subsequent disposal will still be necessary.

The enhanced oil recovery (EOR) studies of Hill et al. (1973) concentrated on displacing crude oil with a flooding medium and decreasing the

"surface tension" between the phases, as do most EOR methods. The technique might work for a soil highly contaminated with a hydrophobic hazardous waste. As an example of tertiary EOR, Hill et al. (1973) described the development of an aqueous surfactant system for recovering Far Springs crude oil in Benton, Illinois. Petroleum sulfonate was selected as the surfactant because of the wide range of types commercially available and their low cost. The addition of sodium chloride to the 3.1 percent active surfactant further lowered the interfacial tension between the crude oil and the aqueous solution. A sequestering agent, sodium tripolyphosphate, was included to further improve compatibility with Benton reservoir water. Once the surfactant-oil emulsion slug was injected, a higher viscosity water wash containing a soluble polymer (such as Dow Pusher 520) was introduced to achieve a stable plug flow displacement. A final water drive completed the recovery. This tertiary recovery approach is an example of using water with a combination of surfactants as described earlier.

A unique approach for in situ removal of hazardous wastes from soils is to employ micellar solution flooding, another tertiary oil recovery technique. Micellar solution flooding is a process in which a solution containing a surfactant-stabilized dispersion of water and hydrocarbons is injected into the oil reservoir. The microemulsion is miscible with both the crude oil and water. After injecting the micellar solution, a high viscosity mobility buffer is injected to protect the emulsion from degradation by the drive water. The composition of typical micellar material, e.g., Richburg Micellar Solution, is as follows:

Water	68.03%
Diesel Oil	17.97
Witco Sulfonate TRS 16	5.46
Witco Sulfonate TRS 40	5.51
Amyl Alcohol	2.37
Butyl Alcohol	0.66

For removal of various hazardous hydrophobic organics from the soil matrix, the development of compatible micellar solutions for hazardous wastes could be explored.

Chou et al. (1982) studied the effect of soluble salts and caustic soda on the solubility and adsorption of hexachlorocyclopentadiene on soils. While increasing the concentrations of brine, sodium chloride, and sodium hydroxide caused an increase in adsorption, sodium hypochlorite caused a slight decrease. The salts causing the greatest depression in solubility also caused the greatest increase in adsorption. No explanation was given for the reduced adsorption caused by the sodium hypochlorite, but more intensive study may be warranted.

2.1.2 Slightly Hydrophilic Organics

The in situ treatment of slightly hydrophilic organics will probably require water injection/recovery systems using additives, followed by final treatment above ground. The EOR methods presented above for hydrophobic organics should also be applicable to slightly hydrophilic organics.

To date, the primary efforts to remove benzene, toluene, and other slightly water-soluble floating aromatics from releases to the saturated/unsaturated interface has been by a water injection/recovery system. If necessary, in a drawdown well, the floating organics are skimmed from the groundwater while still in the well and recovered independently. The water layer containing only dissolved organics is pumped from the well and the organics are removed by a combination of air stripping plus activated carbon.

In a recent study, Dragun and Helling (1982) reported soil- and clay-catalyzed reactions of organic chemicals, such as benzene and ethyl-benzene, through free-radical oxidation. These reactions occur most often in a well-aerated soil environment; therefore, they would be important if in situ microbial oxidation were considered.

An approach for treating low water solubility chlorinated organics in place is reaction with sodium polyethylene glycolates (NaPEG). Pytlewski et al. (1980) first demonstrated in the laboratory that NaPEG could effectively dechlorinate PCBs to form possibly reusable materials. At USEPA/HWERL-CINN, Rogers has recently initiated laboratory and field studies on the use of NaPEG as a spray-on reagent for treatment of chemically contaminated low moisture soils. Using the NaPEG reaction to treat chlorinated organic hazardous material may be limited to aboveground destruction of partially dried chlorinated aromatic materials. Another possibility might be an in situ reaction within a partially dried area around a chlorinated organic waste site. The drying could be achieved by a combination of containment, including covering with a surface cover, and underground forced air drying with removal of vaporized organics prior to surface venting.

2.1.3 Hydrophilic Organics

Water injection/recovery systems for hydrophilic organic soil contaminants such as phenols and alcohols would not require surfactants or other additives to recover the contaminants. The high water solubility of hydrophilics is usually also accompanied by low adsorptivity on soil, due to the polar nature of the molecules. The use of an alkali in the water could, however, improve the solubility of phenols (which are weak acids) in water.

2.1.4 Heavy Metals

Releases of heavy metals from uncontrolled hazardous waste sites might be mitigated using an injection/recovery system or an injection system alone to precipitate the metals in place or to remove dissolved cations using a water wash or a buffered water wash. In an earlier study, Huibregtse and Kastman (1978) proposed using a water wash followed by dilute sodium sulfide to precipitate metallic sulfides in place. However, it was only recently that Pohland et al. (1981, 1982) substantiated the high stability of many heavy metal sulfide precipitates in soils. Their results showed that the solubility data, combined with the persistence of low levels of dissolved sulfide anion, provided confirming evidence that the sulfide should be the controlling precipitation mechanism in landfills. According to USEPA (1979), the low solubility of the sulfide precipitate has resulted in increased acceptance of

these techniques especially where more stringent control of the dissolved metal is required. For soil treatment, a sodium sulfide or sodium hydrosulfide solution would be injected, with a buffer if necessary to maintain sufficient sulfide ion concentration. An important potential concern is that the sulfide precipitation will obstruct the soil pores and diminish the flow rate. Reaction conditions would have to be adjusted to produce the finest sulfide precipitates possible to minimize clogging of soil pores.

Another approach to stabilizing electroplating sludge is to combine electroplating waste with municipal solids. Studies by Myers et al. (1980), Phung et al. (1982), Kinman et al. (1982), and Jones and Malone (1982) have been mostly favorable, although testing is still in progress and the chemistry has not been thoroughly explained or documented.

Finally, leaching to remove heavy metal compounds using chelates or acidified solutions and an injection/recovery system would be feasible. However, removal of large quantities of heavy metal contaminants from a waste site would require an efficient aboveground treatment system to concentrate the spent leaching solutions before disposal.

2.2 POTENTIAL PILOT-SCALE, AND FULL-SCALE TESTS OF SOIL COUNTERMEASURES

The previous subsection focused on laboratory and pilot-scale findings disclosed in the literature and appropriate ideas for laboratory testing. Based on these findings, a range of scaled-up studies is discussed here that can serve as models for studying in situ treatment of hazardous releases from uncontrolled waste sites and spills.

2.2.1 Pilot-Scale Testing

Table 6 lists examples of scaled-up testing arrangements. The table lists selected references that discuss the scale-up advantages and disadvantages. Table 6 has been subdivided into three types of scale-up: pilot testing in disturbed soils, modeling and verification using computer simulation, and full-scale controlled condition testing in undisturbed soils.

To date, pilot-scale column tests [using columns 15 cm (6 in) to 305 cm (10 ft) in diameter] have been oriented toward co-disposal of heavy metals with municipal waste. The justification for using larger columns for these plug flow tests has been the need to secure a large representative sample of municipal refuse and the desire for better measurement and control of the test procedure. De Poorter and Hakonson (1981) conducted tests with low level radioactive wastes on a large scale for better measurement and sampling without disturbing the long-term results of their low level contamination test program. In general, the larger column tests have the advantages of reduced wall effects; improved instrumentation, monitoring, and sampling capability; adaptability to handle a heterogeneous waste mixture; and practicality of carrying out the testing in an exposed, more natural environment. The disadvantages of large column tests are that costs are high, testing is nearly one-dimensional, and ultimately, more hazardous waste will have to be disposed afterward.

TABLE 6. SCALE-UP OPTIONS FOR TESTING IN SITU TREATMENT METHODS

	Selected References
Pilot Testing (Disturbed soils primarily)	
Pilot-scale column tests (15-305 cm diameter)	Myers et al. (1980), Phung et al. (1982), Kinman et al. (1982), Jones and Malone (1982), De Poorter and Hakonson (1981)
Pilot-scale box tests (Three-dimensional)	Texas Research Institute (1979, 1982b) Huibregtse et al. (1978) Huibregtse and Kastman (1978)
Modeling and Verification	
Pilot-scale model (Three-dimensional)	Garon et al. (1980) [fireflooding-EOR] Huygen and Lowry (1979) [steamflooding-EOR]
Full-Scale Testing (Undisturbed soils)	
Simulated release tests with surrogates (In situ containment and treatment unit as delivery/system)	Rollinger (1978), Huibregtse and Kastman (1978)
Sites of opportunity	
--Superfund sites	USEPA (1984a)
--Other uncontrolled hazardous waste sites	
--Spills	Harsh (1978), Winn and Schulte (1982)

Pilot-scale box tests provide the capability to conduct tests on a three-dimensional scale. The Rexnord studies (Huibregtse et al., 1978; Huibregtse and Kastman 1978) included tests in a sand box that was 122 cm (4 ft) deep, 107 cm (3.5 ft) wide, and 152 cm (5 ft) long. The very high recoveries of contaminants from the testing suggest that the adsorption capacity of the sand may have been very low. The Texas Research Institute studies (1979, 1982b) on surfactant-enhanced gasoline recovery were conducted in a 3 m x 3 m x 1.2 m deep sand-filled concrete tank with a nominal 0.3 m deep, 3 percent gradient water table. These studies showed a greater spread of results with recovery markedly improved by daily percolation or injection of surfactant.

In general, larger pilot-scale box tests such as those used by the Texas Research Institute provided the advantages of testing in a facility with the following capabilities:

- o Three-dimensional tests at a scale approaching the field
- o Water table with gradient
- o Time cycle for weather conditions
- o Sampling and monitoring easily implemented
- o Leakage collection
- o Moderate soil waste generated.

Conversely, only limited pilot-scale box testing has been conducted on the larger scale (Texas Research Institute 1979, 1982b), so the interpretation of results and scale-up value, although encouraging, cannot be compared with other findings.

Three-dimensional pilot-scale model testing has been applied to fire-flooding and steamflooding for enhanced oil recovery (see Table 6). One goal of the testing was to establish a basic understanding of the mechanisms in order to validate numerical models. Although the results were useful, the modeling techniques may not directly apply to chemical countermeasures studies.

2.2.2 Site of Opportunity Testing

The application of chemical countermeasure techniques at a site of opportunity has been very limited. The main reasons are caution and scarcity of experience in implementing in situ countermeasures to hazardous release problems. For example, according to a USEPA survey completed by Neeley et al. (1981), of 180 remedial actions (on 169 sites), there were only two instances in which in situ treatment was used. In one case, lime was added to a phenol waste and in another phosphates were added to accelerate biodegradation of a gasoline spill. Purging wells or interception ditches were used in 15 examples, with or without surface treatment, to prevent groundwater contamination from landfills.

A case study review on remedial actions at 23 hazardous waste sites has been published by the EPA (1984). This included several studies on use of slurry walls and direct recovery techniques for removing groundwater contaminants. Of considerable interest was the system used by O.H. Materials, Findlay, OH, at the Goose Farm site in Plumstead Township, NJ. O.H. Materials worked closely with the Department of Environmental Protection (NJ) and used

a spray irrigation and well-point collection system with aboveground treatment to remove the contaminants from the groundwater. The treatment consisted of a carbon adsorption system to remove organics, a clarifier, a four-cascade aqueous carbon treatment system, aeration to strip organics not treated by carbon, and an effluent storage tank. The treated groundwater was reinjected. Determining the magnitude and severity of groundwater contamination, particularly in highly permeable soils (sand), may require installation of extensive monitoring wells and the development and implementation of a staged cleanup.

Spills of hazardous waste have resulted in the rapid development and implementation of technology to treat these wastes in place. Harsh (1978) documented the in situ neutralization of acrylonitrile by first raising the pH of the contaminated area above 10 with lime, and then spraying sodium hypochlorite over the area. This treatment was successful, although the water sprayed over the area in fighting the fire aggravated the contamination problem.

The field techniques that would be applicable to in situ cleanup of soils would be:

- Water and chemical additive injection or surface spraying, followed by recovery using a drawdown well system (hydrodynamic control) or possibly an interceptor trench, or French drains downgradient from the source; leachate treatment would be conducted above ground
- in situ precipitation using an injection system with or without a recovery system
- in situ fixation process with an injection system if needed, but probably no recovery system
- in situ chemical reaction or degradation using an injection system with or without a recovery system.

SECTION 3

CONCLUSIONS

The laboratory research was conducted to determine whether significant improvements to *in situ* cleanup of contaminated soils could be obtained using aqueous surfactants rather than just water (the only cleanup method demonstrated to date). Further laboratory development of the surfactant countermeasure included optimizing the concentration of surfactant used for cleanup, and development of contaminated leachate treatment methods to enable reuse of the surfactant.

The aqueous surfactant countermeasure was tested in the laboratory using two basic methods. The first method was shaker table agitation, to quickly determine the soil/aqueous surfactant partitioning of the model contaminants under differing conditions. Shaker studies measured cleanup under conditions permitting equilibration of the contaminants between soil and solution. After the shaker table tests, cleanup was measured under gravity flow conditions using soil column tests. These tests took much longer to run, but were necessary to verify the cleanup behavior of the aqueous surfactant under conditions resembling field use. Besides the optimum surfactant concentration, the effects of leachate treatment and recycling were also studied using soil column tests, to minimize the hazardous waste generated upon scale-up.

3.1 EFFECTIVENESS OF THE SURFACTANTS

Based on bench-scale tests designed to screen potential surfactants for use as *in situ* soil washing enhancers, a 1:1 blend of Adsee® 799 (Witco Chemical Corp.) and Hyonic® NP-90 (Diamond Shamrock) was found to be an effective combination because of adequate solubility in water, minimal mobilization of clay-sized soil fines (to maintain soil permeability), good oil dispersion, and adequate biodegradability.

Shaker table and column experiments with this blend of surfactants dissolved in water at a total concentration of 4.0 percent (v/v), showed that they were effective in removing 93 percent of the hydrocarbon and 98 percent of the PCB pollutants from contaminated soil. These removals are orders of magnitude greater than those obtained with just water washing and represent a significant improvement to the efficiency of existing technology. Chlorinated phenols were readily removed from the test soil by water washing alone.

Shaker table experiments conducted to determine the optimum surfactant concentration for soil cleanup, with PCB and petroleum hydrocarbon (Murban) contaminated soils, showed the optimum concentration to be 1.5 percent total

surfactant. Individual surfactant concentrations of 0.25 percent or less were unacceptable for effective soil washing, and surfactant concentrations above 0.75 percent were excessive, since no significant enhancement of clean-up resulted. In addition, similar partitioning between soil and surfactant solution by the two pollutant types suggests that the results which would be obtained in further large-scale experiments with the low toxicity hydrocarbons in a fuel oil like Murban might reliably model the behavior of other more toxic hydrophobic pollutant groups, such as PCBs.

The experiment which evaluated the effect of leachate recycling, with treatment applied to the PCB leachate between cycles, showed that:

- Soil cleanup with 1.5 percent total surfactant is good, with less than 1 percent of the PCB remaining on the soil
- The product of hydrolysis represents a relatively small volume (about 12 percent of the total mass of leachate) of highly contaminated material, which can be further treated by incineration, or disposed of for a minimal cost
- The use of the same water for repeated cycles precludes the generation of large volumes of waste leachate
- The final treated water after four cycles contains less than 0.0005 percent of the initial contamination encountered in the soil.

3.2 EFFECTS OF THE TEST SOIL

The efficiency of cleanup of the hydrophobic organic contaminated Freehold soil by the aqueous surfactant solution was directly affected by the low natural organic carbon content of the soil. The low TOC (0.12 percent) represented little organic matter in the soil to adsorb the organic pollutants spiked onto the soil, so the contaminant removal could be expected to be relatively easy compared to a soil with, for example, a 1 percent TOC. However, while the removal of hydrophobic organics from a 1 percent TOC soil using the Adsee® 799 - Hyonic® NP-90 surfactant pair might be difficult, the surfactants would probably be effective for removing chlorophenols, water alone would not work nearly as well as with the low TOC Freehold soil.

The hydraulic conductivity of the Freehold soil as it was packed in the soil columns, which was measured at 1.05×10^{-3} cm/sec, would be practical for field implementation of the countermeasure. However, the time required for a pore volume of surfactant solution to flow through the soil should be considered. With this hydraulic conductivity, if surface flooding were used to obtain saturated conditions from the surface to a groundwater depth of 10 m (32.8 ft), and assuming a porosity of 50 percent, the maximum possible hydraulic velocity would only be about 1.8 m/day, or 13 m/wk (42 ft/wk). And, it would take 5.5 days for one pore volume of solution to flow through the soil from surface to groundwater. A flow rate under similar conditions, with a soil permeability of 1×10^{-4} cm/sec, would yield flow rates of about 1.2 m/wk, which is probably a practical lower limit for the method.

The type of soil most likely to have the required hydraulic conductivity, which is considered moderate permeability, would be a sandy soil or a sandy loam, relatively low in silt and clay or being poorly sorted with respect to grain size. If the soil had zones of low permeability, such as clay horizons or clay lenses, the effects of even a low degree of clay particle mobilization and redeposition by the surfactant could decrease flow rates and treatment effectiveness significantly.

3.3 POTENTIAL TARGET CONTAMINANTS

The type of hazardous chemical for which the surfactant countermeasure was more effective than just water included hydrophobic organics (the PCBs, and the aliphatic hydrocarbons in the Murban fraction) and slightly hydrophilic organics (the aromatic hydrocarbons in the Murban). The chemicals for which the method would probably not be applicable would be heavy metal salts and oxides, or cyanides. The method is not needed for slightly hydrophilic organics, including chlorophenols, unless the soil had a higher natural TOC. For hydrophilic organics such as low molecular weight alcohols, amines, and acids, water alone will usually be sufficient for soil cleanup.

3.4 EFFECTIVE TREATMENT METHODS

Conservation of both water and surfactant prompted the investigation of leachate reuse or recycling. Recycling of the untreated leachate is unacceptable because portions of the soil that have been previously cleaned will be recontaminated rapidly by the introduction of spent leachate.

The desire to recycle surfactants and the large volumes of contaminated leachate generated during soil washing required investigations into the treatment and concentration of the contaminants contained in the leachate. The ideal treatment method would remove and concentrate the contaminants while leaving the surfactants behind for further use. However, the same chemical and physical properties of the surfactant mixture used that act so well to extract the pollutants from the soil also inhibited separation of the contaminants from the surfactants. Due to the high (percentage) level of surfactant contained in the leachate, most of the treatment methods evaluated were ineffective. The best treatment that could be obtained removed both surfactants and pollutants, leaving clean water behind for possible reuse or easy disposal. A summary of methods and their potential for leachate treatment follows:

- Hydrolysis -- Very effective as a primary treatment method for removing both the surfactant and the contaminants.
- Foam fractionation -- Unsuitable for primary treatment due to the elevated (above the critical micelle concentration) levels of surfactant in the leachate; quite suitable as a secondary treatment step.
- Adsorption onto solids -- Of eleven different sorbents tested, including activated carbons, clays, etc., due to the surfactants

present, none adsorbed contaminant well enough for primary treatment; adsorption onto activated carbon should be effective as a secondary treatment step after initial surfactant removal by other means (e.g., hydrolysis).

- Ultrafiltration -- After only limited testing, this approach appeared to be another possible primary treatment method and should be evaluated further.

Hydrolysis followed by adsorption onto activated carbon was the most effective treatment method for leachate generated by the aqueous surfactant countermeasure. However, none of the methods evaluated was successful in effectively separating out the surfactants alone.

SECTION 4

RECOMMENDATIONS

4.1 SELECTING SURFACTANTS FOR IN SITU SOIL CLEANUP

Additional surfactant tests are warranted before this technology can be applied in the field. The surfactant combination used was water soluble, and effective in soil column studies with both the Murban distillation fraction and PCB pollutant groups. Furthermore, the combination allowed good soil percolation rates, as the mixture did not resuspend a significant amount of the clay-sized particles in the soil, thereby inhibiting flow. These characteristics are definitely important; however, for this technology to be cost-effective, reuse of the surfactant is equally important. Accordingly, it is recommended that other surfactants/surfactant combinations be evaluated that have the same "flushing" characteristics but are also more amenable to separation for reuse. Also, the surfactant screening tests for solubility, clay dispersion, and soil dispersion should be followed by mutagenicity tests to ascertain that any surfactants used for larger scale/field testing (and ultimately in actual release situations) do not make the situation worse than the original situation by the application of an additional chemical.

During the soil column studies with these pollutant groups, there was a marked decrease in soil percolation rates with time and accumulated leachate volume. Therefore, in any laboratory, test tank, or controlled condition field testing it seems advantageous to limit (or eliminate) any initial water rinses and initiate aqueous surfactant treatment immediately to effect the maximum soil decontamination before the percolation rate decreases. Also, it may be possible to reduce the total amount of surfactant solution volume and still obtain acceptable soil cleanup. Very significant soil cleanup of Murban hydrocarbons and PCB mixtures was obtained after as little as five pore volumes of aqueous surfactant had passed through the soil columns.

4.2 TESTING OTHER SOILS

The total organic carbon in the Freehold soil was very low (0.12 percent by weight), and numerous studies (Lyman et al., 1982; Karickhoff, 1981; Tinsely, 1980) have indicated that the percentage of organic carbon has a critical effect on the degree of pollutant adsorption. Furthermore, the cation exchange capacity (CEC) was 8.6 milliequivalents per 100 gms, an extremely low value, confirming the absence of mineralogic clay in the soil. If additional laboratory or tank testing were to be undertaken, a second soil type with greater percentages of organic carbon, with mineralogic clay, and/or higher CEC values might be considered to expand the overall applicability of the program results to a broader variety of soil matrices.

4.3 DEVELOPING LEACHATE TREATMENT METHODS

Additional efforts should be directed toward optimizing feasible and cost-effective methods of leachate treatment and in particular separation of the surfactant for reuse. Specifically, ultrafiltration appears promising and warrants further investigation; foam fractionation should also be investigated further. The use of equipment and technologies already existent should be examined in greater detail to minimize scale-up costs.

4.4 FURTHER COUNTERMEASURE DEVELOPMENT BEFORE FIELD USE

The testing of a new technique, in which hazardous contaminants are rendered more mobile, presents a potentially greater environmental threat unless the tests can be readily stopped at any point as required to permit the immediate remedy of any failure by established techniques. Because the aqueous surfactant countermeasure is still developmental, the field tests should be conducted on a reduced scale until the procedures are proven workable and the important parameters are understood and controlled.

The laboratory tests have established the effectiveness of the technique for soil cleanup sufficiently to justify tests on a larger scale. Pilot-scale (test tank) possibilities for testing the countermeasure are described under the Information Search Section. Pilot-scale testing would require the use of disturbed soil, and would probably not further the development of the method as much as controlled condition field testing at a site of opportunity.

An appropriate site for field testing would have the following characteristics:

- Moderate to high permeability (coefficient of permeability of 10^{-4} cm/sec or better)
- Small size (e.g., 30 m x 30 m x 10 m deep)
- Minimal immediate threat to drinking water supplies
- Hydrophobic and/or slightly hydrophilic organic contaminants
- Concentrated contamination source removed or controlled
- Low to moderate natural organic matter content in soil (TOC 0.5-2 percent).

If either small sites, or physically separated sections of a large site (e.g., with a slurry or grout wall) were selected, the aqueous surfactant countermeasure described in this report could be applied, tested further, and improved to a point of full field countermeasure applicability.

The hydrostatic pressure during all of the column tests was relatively low: about 60 cm. The flow rate could be increased significantly, thereby reducing treatment times, if the hydrostatic head of the treatment solution were greater.

SECTION 5

MATERIALS AND METHODS

5.1 SOIL SELECTION AND CHARACTERIZATION

In choosing a soil to be used in the surfactant washing tests, the applicability of the results to actual field situations was a primary consideration. The selection process included identifying the native soils at each of the Region II Superfund sites for which data was available, determining the most commonly occurring soil type series, and locating a soil of the same soil taxonomic classification which could be excavated and used in the testing experiment. The limited availablity of published soil surveys and the fact that some of the sites were mapped only as "urban land," which indicated that the original soil had been altered or removed, reduced the number of Superfund sites for which information could be gathered to 10 sites. Supplementary data for the D'Imperio, Price, and Lipari Landfill sites were obtained from the Region II Superfund site investigation files located in the New York City Regional office.

Each site's exact location was ascertained using topographic maps and information supplied in the Field Investigation Team (FIT) report summaries. Next the site was located on soils maps contained within Soil Survey Reports compiled by the U.S. Department of Agriculture (USDA) Soil Conservation Service (SCS). The soils indicated within a radius of two times the square root of the total area of each site were identified. If more than five different soil series were present, the five major soils in terms of area were chosen. Table 7 lists the soils series as well as the taxonomic classification to the subgroup level according to Soil Taxonomy (Soil Survey Staff, 1975) for the soils encountered at the Region II Superfund sites. Also outlined within Table 7 are the textural classes and permeability ranges for each soil series. The most commonly occurring classification was Typic Hapludults, fine- to coarse-loamy. An explanation of the nomenclature is as follows:

Typic	Representative of the great group
Hapl	Great group element meaning "simple or minimum horizons"
ud	Suborder element meaning "of humid climate"
ults	Of the order Ultisols: the soils have an argillic horizon, i.e., a zone of clay accumulation, and have low base saturation.

The coarse-loamy textural class indicates a soil with a low content of clay (less than 18 percent) and a high content (more than 15 percent) of fine,

TABLE 7. SOILS OF TEN REGION II SUPERFUND SITES

Site	Soil Series	Taxonomic Classification	Texture	Permeability*
Lipari Landfill	Aura	Typic Hapludults	fine-loamy	moderately slow to moderate
	Sassafras	Typic Hapludults	fine-loamy	moderate to moderately rapid
D'Imperio	Matawan	Aquic Hapludults	fine-loamy	moderately slow to moderate
	Klej	Aquic Quartzipsamments	sandy	rapid to very rapid
	Woodstown	Aquic Hapludults	fine-loamy	moderate to very rapid
	Pocomoke	Typic Umbraquults	coarse-loamy	moderate to moderately rapid
	Sassafras	Typic Hapludults	fine-loamy	moderate to moderately rapid
Price	Downer	Typic Hapludults	coarse-loamy	moderate to moderately rapid
	Klej	Aquic Quartzipsamments	sandy	moderate
	Sassafras	Typic Hapludults	fine-loamy	moderate to moderately rapid
Facet Enterprises	Howard	Glossoboric Hapludalfs	loamy-skeletal	moderate
Love Canal	Canandaigua	Mollic Haplaquepts	fine-silty	moderate
	Madalia	Mollic Ochraqualfs	fine (30-60% clay)	moderate
Bridgeport Brothers	Sassafras	Typic Hapludults	fine-loamy	moderate to moderately rapid
	Downer	Typic Hapludults	coarse-loamy	moderate to moderately rapid
	Dragston	Aquic Hapludults	coarse-loamy	moderate
	Klej	Aquic Quartzipsamments	sandy	moderate
	Woodstown	Aquic Hapludults	fine-loamy	moderate
Moira	Coveytown	Aeric Haplaquents	sandy/loam	moderately rapid to rapid
	Scarboro	Histic Humaquepts	sandy	rapid to very rapid
	Walpole	Aeric Haplaquepts	sandy	moderately rapid
	Empeyville	Aquic Fragiorthods	loam	slow
	Fahey	Aquentic Haplorthods	sandy-skeletal	rapid
Niagra Co. Refuse	Canandaigua	Mollic Haplaquepts	fine-silty	moderate
	Raynham	Aeric Haplaquepts	coarse-silty	moderate to moderately rapid

(continued)

TABLE 7. (continued)

Site	Soil Series	Taxonomic Classification	Texture	Permeability*
Pollution Abatement Services	Scriba	Aeric Fragiaquepts	coarse-loamy	slow
	Ira	Typic Fragiochrepts	coarse-loamy	slow
	Sodus	Typic Fragiochrepts	coarse-loamy	slow
Helen Kramer Landfill	Freehold	Typic Hapludults	fine-loamy	moderate

*Terms used to describe permeability are as follows:

Very slow <4.2×10^{-5} cm/sec
Slow 4.2×10^{-5} to 1.4×10^{-4} cm/sec
Moderately Slow 1.4×10^{-4} to 4.2×10^{-4} cm/sec
Moderate 4.2×10^{-4} to 1.4×10^{-3} cm/sec
Moderately Rapid 1.4×10^{-3} to 4.2×10^{-3} cm/sec
Rapid 4.2×10^{-3} to 1.4×10^{-2} cm/sec
Very rapid >1.4×10^{-2} cm/sec

medium, and coarse sands plus coarse fragments up to three inches. Fine-loamy is the same as above except that clay content is 18 to 35 percent. Table 8 outlines the frequency of occurrence of the various soil subgroups and permeability ranges for each.

TABLE 8. MOST COMMON SOIL SUBGROUPS AT REGION II SUPERFUND SITES

Soil Subgroup	Range of Permeability	Frequency of Occurrence *
Typic Hapludults	moderately slow to moderately rapid	10
Aquic Hapludults	moderately slow to very rapid	4
Aquic Quartzipsamments	moderate	3
Mollic Haplaquepts	moderate	2
Aeric Haplaquepts	moderate to moderately rapid	2
Typic Fragiochrepts	slow	2
Typic Umbraquults	moderate to moderately rapid	1
Aeric Haplaquents	moderately rapid to rapid	1
Aquentic Haplorthods	rapid	1
Mollic Ochraqualfs	moderate	1
Aeric Fragiaquepts	slow	1
Typic Rhodudults	moderate	1
Histic Humaquepts	rapid to very rapid	1
Glossoboric Hapludalfs	moderate	1

*of 10 sites studied

In addition to taxonomic classification, other factors were considered in choosing the soil for surfactant tests. A permeability rating of 10^{-2} to 10^{-4} cm/sec was considered an acceptable range; less permeable soils would take too long to test. Also, the soil could not contain significant amounts of the clay of marine origin called glauconite. The glauconitic soils found in the Coastal Plain of Region II are known to lose their permeability upon wetting.

The soil selected for use in the study was a Freehold series typic hapludult from Clarksburg, New Jersey. Initial characterization of the soil, consisting of grain size analyses, determination of natural moisture content, compaction tests, and permeability vs density tests, was conducted by Raamot Associates, Parlin, NJ. Mineralogy by X-ray diffraction was undertaken by Technology and Materials Company, Santa Barbara, CA, on a Phillips Electronics X-ray diffractometer; the X-ray diffraction charts were interpreted by comparison with standard diffraction file data. The total organic carbon content (TOC) was measured by Laucks Testing Laboratories, Inc., Seattle, WA, according to EPA Method 415.1. Laucks Testing Laboratories, Inc., also determined the cation exchange capacity of the soil using the method of Jackson (1960).

5.2 SURFACTANT SCREENING TESTS

The surfactant combination used by Texas Research Institute for flushing gasoline from sand (TRI, 1979), Richonate®-YLA and Hyonic® NP-90 (formerly called Hyonic® PE-90), was screened along with several other surfactants and surfactant combinations for three critical characteristics:

- o Water solubility (deionized water)
- o Clay particle dispersion
- o Oil dispersion.

Any candidate surfactant must dissolve in water to form an effective solution for in situ cleanup. Deionized water was used to test the solubility because it was available in quantity and had constant physical and chemical characteristics. The laboratory tap water varied greatly in salts content from week to week.

Preliminary soil column tests with the Richonate®-YLA and Hyonic® NP-90 surfactant combination showed constantly decreasing flow rates; this was attributed to clay-sized particle mobilization and redeposition by one or both surfactants. To minimize this effect, and to assist in selection of another surfactant combination other than the one used by TRI, screening tests for clay dispersion were run. A 250 mg sample of the Freehold soil was shaken on a wrist action shaker with 10 ml of the surfactant solution for 5 minutes in a 15 ml screwcap vial, then allowed to settle overnight. The cloudiness of the solution was noted as an indication that the clay was still suspended.

The ability of the chosen surfactant(s) to disperse a hydrophobic organic like an oil (Prudhoe Bay crude was used for the test) was considered an accurate model for the ability to clean organics from soil. A 50 ml aliquot of the surfactant solution was swirled in a 100 ml beaker with two drops of oil, and the extent of oil dispersion was determined by the cloudiness and darkness of the solution.

5.3 SHAKER TABLE TESTS

To represent the approximate levels found at waste sites (Section 2, Information Search), soils were spiked with 100 ppm PCB, 1000 ppm Murban

distillation fraction, and 30 ppm chlorophenol for shaker table studies by the following procedure. The amount of soil necessary for one set of shaker table samples was spread evenly in aluminum pans to a depth of approximately 1.3 cm (0.5 in) and spiked with an aerosol spray of the required amount of contaminant mixture dissolved in methylene chloride. The methylene chloride was allowed to evaporate, and the soil was mixed by stirring in the pans, then stored in sealed containers. Approximately 100 g of the contaminated soil was weighed into each of the 500 ml Teflon jars. In preparing soil for flow-through column studies each of the nine portions of soil (lifts) of 775 g each was spiked as described above and then packed into the column as described in the next section.

Shaker table partitioning experiments were conducted to determine the effects of various surfactant concentrations on soil cleanup. After spiking the Freehold soil with PCBs or hydrocarbons, various concentrations of surfactants in water were used to wash the soil under well-shaken conditions allowing equilibration of the contaminants between the soil and the surfactant solution.

The procedure for conducting the shaker table tests was as follows. One hundred grams of contaminated soil was agitated with 200 ml of the appropriate surfactant concentration on a shaker table for 1 hour, then centrifuged for 15 minutes at 2500 revolutions per minute (rpm). The leachate was decanted and both soil and leachate were analyzed for the contaminants. Leachates and soils were extracted and analyzed according to the methods described in Section 5.5, Analytical Procedures. The results of these experiments can be found in Section 6.3, Preliminary Soil Column Experiments.

5.4 SOIL COLUMN TESTS

The custom fabricated soil columns used in this study were 7.6 cm (3 in) I.D. by 150 cm (5 ft) glass columns. Both ends of the column were sealed with nippled glass caps. A Teflon O-ring, placed between the glass column and cap, sealed the two surfaces as they were crimped together by an adjustable stainless steel jacket. Teflon tubes connected to the end caps allowed the introduction of the aqueous surfactant solutions and the collection of leachates.

At the initiation of each experiment, using one pollutant mixture, a series of columns was prepared. Contaminated soil was packed into the columns using the following procedure. After leak testing the column with deionized water, a plug of glass wool was inserted at the top of the column and pushed down to the bottom using the compaction device. A lift of soil weighing approximately 775 g was then added to the column and packed to a height of 10 cm (4 in) using a custom-made controlled drop-hammer compactor designed to fit inside the column. Figure 1 shows the addition and compaction of one lift of contaminated soil. Following compaction of each 10 cm lift, the soil was tested with a pocket penetrometer (Soil Test Model CL-7000, Soil Test, Inc.) modified for use in the 7.6 cm diameter columns. To ensure better cohesion between layers, the upper 0.6 cm (0.25 in) of each plug was scarified before the next lift of soil was placed.

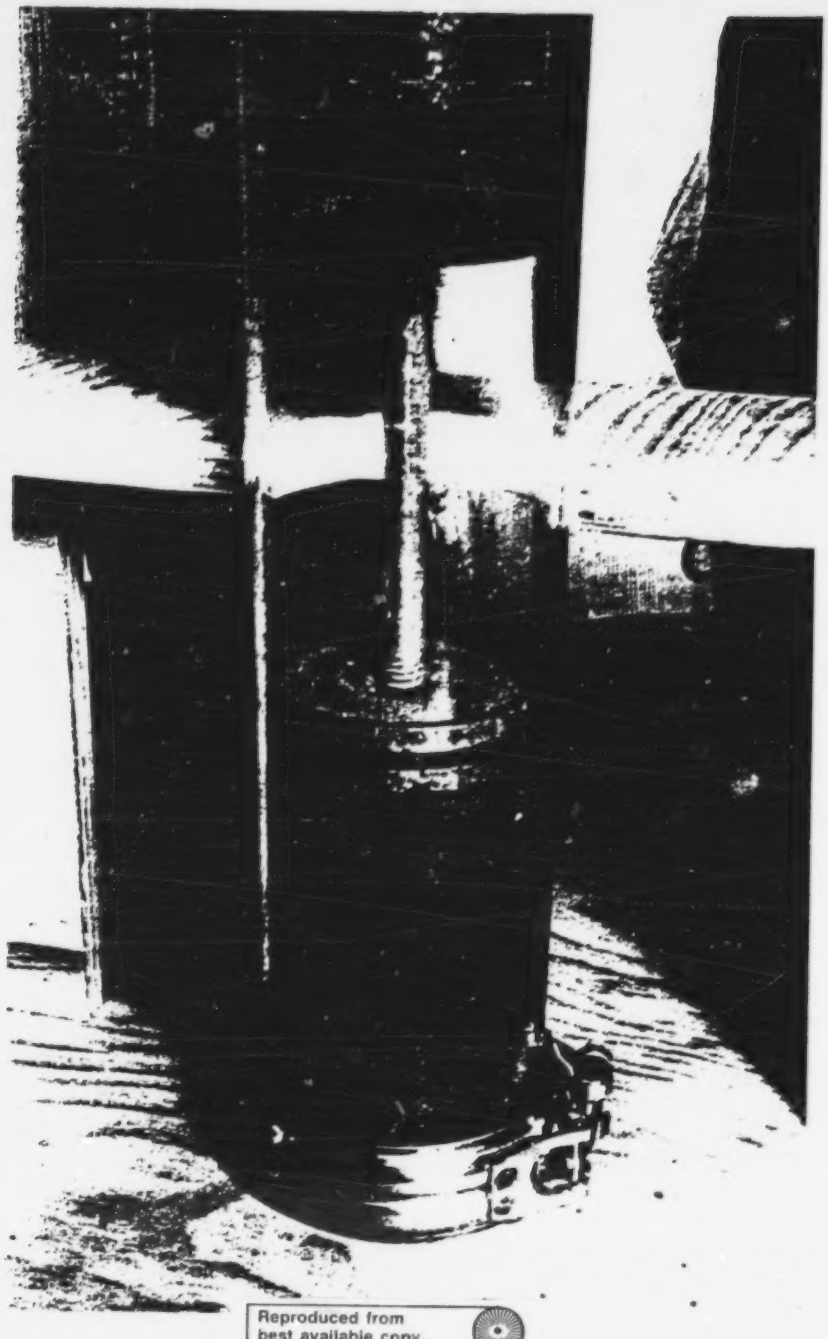

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FIGURE 1. HAMMER COMPACTION DEVICE IN GLASS SOIL COLUMN

Soil weight, packing depth, number of taps required, and compaction data were monitored for uniformity as each column was packed. The soil was packed to a total height of 90 cm (3 ft) and compacted to a density of 1.68-1.76 g/cm^3 (105-110 lbs/ft^3), yielding a percolation rate of 3 to 5 x 10^{-4} cm/sec, which was comparable to the natural permeability measured by ASTM methods (Raamot Associates, 1983). Compaction/density and percolation rate testing in the laboratory demonstrated that this procedure was reproducible. Figure 2 shows a set of packed soil columns, with leachate receiving carboys below, in the standard arrangement for column tests.

The first test, a preliminary experiment with columns of each of the three contaminant mixtures, tested water followed by 4 percent total surfactant for soil cleanup. Four sets of soil column tests were conducted using Murban hydrocarbons, PCBs, and/or chlorophenols spiked soil. The second test was designed to assure that the optimum surfactant concentration under gravity flow conditions was not significantly different from that established under equilibrium conditions. The third column test evaluated the effect of washing soil with recycled, untreated leachate compared to soil washing with fresh surfactant only. The fourth column test evaluated the effects of washing soil with recycled, treated leachate. In each round of column experiments the soil spiking and column packing procedures were identical.

Column tests were run by allowing the surfactant mixture to percolate through the soil column under a 30 cm constant head. Leachate was collected in 20 liter glass carboys; columns were sacrificed after the appropriate number of passes had been administered (one pass was defined as three to four pore volumes). Column sacrifice consisted of allowing the column to drain overnight then scraping the top, middle, and bottom sections out using a specially designed tool. The individual sections from the columns were homogenized prior to extraction; leachate and soil analyses were conducted as described in Section 5.5, Analytical Procedures. The experimental procedures for the four column tests differed, therefore, they are described in detail preceding the results and discussion of each experiment (see Section 6, Results and Discussion).

5.5 ANALYTICAL PROCEDURES

The analysis of contaminated soils and aqueous leachates involved solvent extraction, liquid chromatography (fractionation into aliphatic, aromatic, and polar fractions) and instrumental analysis by a combination of flame ionization detector gas chromatography (FID-GC), electron capture detector gas chromatography (ECD-GC), and high performance liquid chromatography (HPLC). Extraction procedures for the two types of samples that were generated by this study are presented in the next two subsections.

5.5.1 Extraction of Organics from Aqueous Media

The protocols employed for priority pollutant sample preparation involving aqueous media were EPA Methods 608 and 625 (Federal Register, 1979).

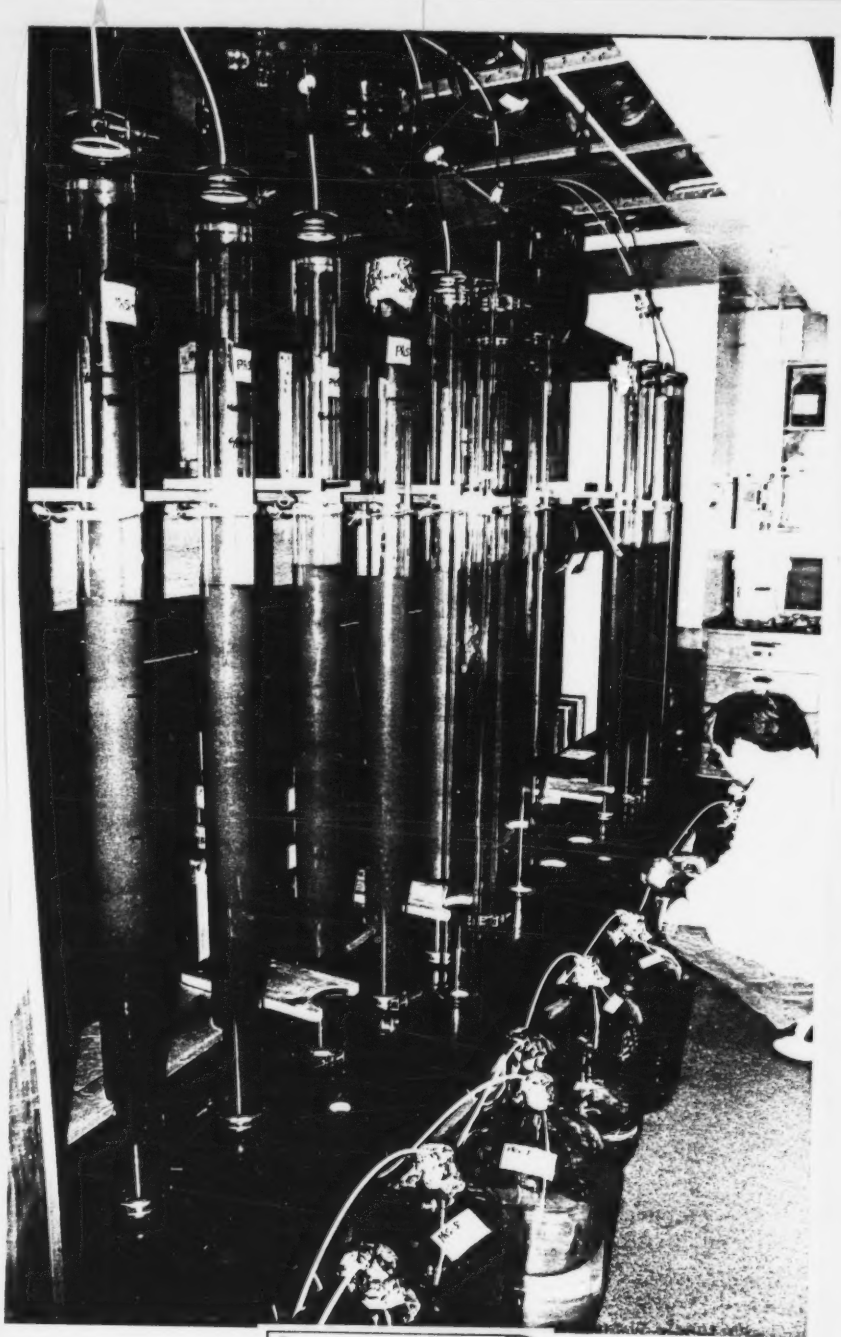

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FIGURE 2. STANDARD SOIL COLUMN
TEST ARRANGEMENT

For leachates in which aromatic hydrocarbons or PCBs were present, EPA Method 608 was followed. Both contaminant types were carried through the sodium sulfate drying step, after which the Murban hydrocarbon extract was subjected to silica gel column liquid chromatography (LC). This LC fractionation scheme is described in detail in subsection 5.5.2, Extraction of Organics from Soil. In this manner, the separate behavior of aliphatic and aromatic Murban hydrocarbons during shaker table equilibration and soil column leaching could be observed. The Murban hydrocarbon contaminant extracts were analyzed by FID-GC.

The extract from the PCB (Arochlor® 1260) contaminant leachate was analyzed by ECD-GC immediately after the sodium sulfate drying step, without silica gel fractionation.

For the leachate-containing chlorinated phenols, EPA Method 625 was utilized. Because the concentration of specific phenolic compounds was being monitored, the base/neutral extraction was omitted. The leachate was subjected to the Method 625 acid/phenol extraction step only, and then analyzed by HPLC.

5.5.2 Extraction of Organics from Soil

Soil samples were prepared for pollutant analysis utilizing a rigorous shaker table extraction procedure which is similar to that described by Payne et al. (1978) and Brown et al. (1980), and which has been shown to yield comparable results to Soxhlet extraction (MacLeod et al., 1982; MacLeod and Fischer, 1980; Payne et al., 1979). This procedure is presented in Appendix A.

The extracts were then concentrated to approximately 1 ml using a K-D evaporator and, for Murban extracts, solvent exchanged to hexane in preparation for silica gel LC separation and analysis by FID-GC. PCB and phenol extracts were analyzed by ECD-GC and HPLC, respectively. No further cleanup steps were necessary for these two pollutant groups.

5.5.3 Instrumental Analysis

The GC and HPLC run conditions and run program specifications, necessary for analyzing each of the three types of contaminants and the surfactants, are presented in Appendix B.

A Hewlett Packard 1084B HPLC was used to analyze for phenols in soil column sediments and leachates. The HPLC was equipped with an HP 79841A Autosampler with a 60 vial sampling capacity. The HPLC was interfaced to a Waters Model 440 absorbance detector set at a wavelength of 280 nm.

Quantifying the surfactants in leachates and treated leachates was accomplished by UV spectroscopy on a Hitachi Model 100-80 UV-VIS spectrophotometer. Linear response was established using a deuterium lamp at a wavelength of 271 nm in the double beam mode of operation. The linear range

for total surfactants (Adsee® 799 + Hyonic® NP-90) was determined to be from 0.001 to 0.20 percent with deionized (DI) water in the reference cell.

Quality control tests were completed to evaluate the extent of interferences due to the presence of PCBs, or the effects of leachate contact with soil, filtration, or centrifugation. Interferences due to these effects were minimal.

5.5.4 Internal Standards

Every sample to be analyzed was spiked with an internal standard mixture. The standards were added to the raw samples in a precise and quantitative manner. They were carried throughout the analytical scheme to check and monitor the recoveries of the compound classes they represented. The main consideration when selecting the compounds to be used as internal standards was their solubility and chromatographic similarity to the compounds of interest; i.e.:

- N-Decylcyclohexane (aliphatic) and hexamethylbenzene (aromatic) were used as internal standards for the Murban hydrocarbon contaminant samples.
- The pesticide Lindane was the internal standard for PCB samples. It behaved similarly to Aroclor® 1260 and gave a separate, distinct peak during GC analysis.
- For the chlorinated phenol test mixture (di-, tri-, and pentachlorophenols), the internal standard was 4-chloro-3- methylphenol. It was an ideal surrogate compound since it exhibited the same chemical behavior as the other chlorophenols, but was not present in the prespiked sample.

The amounts of standards added were in the range of concentrations expected for the analytes. Utilization of these spiked materials as references in analysis of the pollutants of similar structures was necessary for reproducible determinations in samples of widely varying matrices (i.e., aqueous leachate, leachate plus surfactant, and soils).

5.6 LEACHATE TREATMENT

The methods of leachate treatment, which were investigated, included hydrolysis, solid adsorption, foam fractionation, and ultrafiltration. The materials and methods used during these short investigations are presented with the results in subsection 6.4, Evaluation of Leachate Treatment Techniques, to allow easier understanding of the effects that the methods had upon the results.

SECTION 6

RESULTS AND DISCUSSION

6.1 SOIL CHARACTERISTICS

Subsection 5.1, Soil Selection and Characterization, describes how a Freehold series typic hapludult soil was selected for the study. Prior to undertaking shaker table or column experiments, the soil was characterized by grain size, density, percent moisture, porosity, mineralogy by X-ray diffraction, cation exchange capacity (CEC), and total organic carbon (TOC).

Preliminary soil characterizations were completed by Raamot Associates (1983). Grain size analyses, determinations of natural moisture content, and modified Proctor compaction tests were undertaken to develop moisture/density characteristics and determine optimum moisture content for permeability testing at various densities. Figure 3 presents the grain size gradation curve of the Freehold soil following dry sieve analysis. The soil was relatively sandy (83 percent) and low in silt/clay (10 percent). Although the soil was packed in the columns without wetting, its behavior during column tests under saturated conditions was predictable more accurately by wet sieve grain size analysis. Table 9 presents the grain size distribution obtained by wet sieve and pipet analyses.

TABLE 9. GRAIN SIZE DISTRIBUTION BY WET SIEVE AND PIPETTE ANALYSIS

Class	Size Range (um)	Mass (percent)	Estimated Surface Area (percent)
Gravel	>1000	16	<0.5
Sand	62-1000	61	5
Silt	8-62	15	34
Clay	<8	8	61

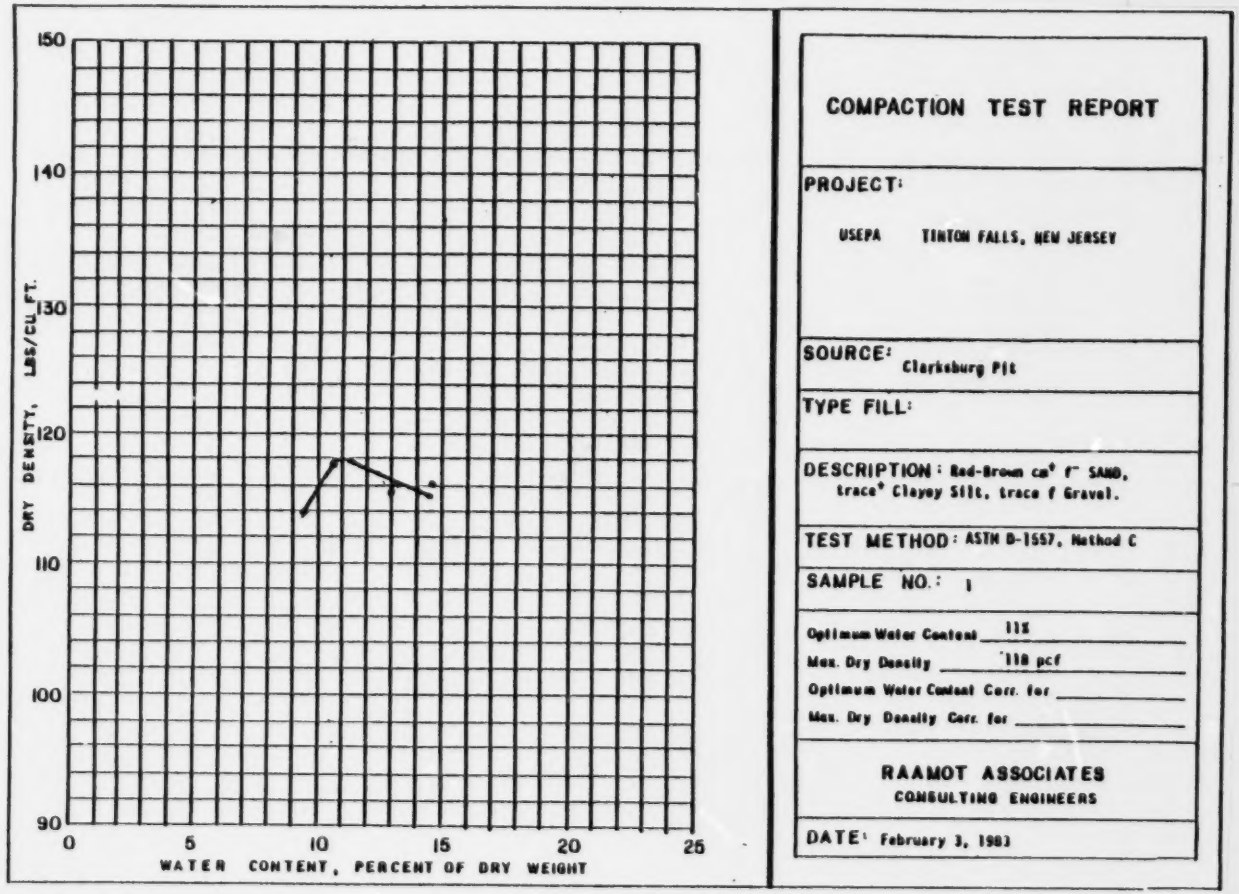

FIGURE 3. STANDARD GRAIN SIZE GRADATION CURVE

As the data illustrate, compared to the dry sieve analyses, significantly higher levels of percent fines (silt, 15 percent and clay, 8 percent) were observed in the wet sieve analyses. The fines tend to limit soil permeability. Approximately 95 percent of the theoretical surface area is represented by these fine particle sizes. The tendency of a soil to adsorb organic contaminants is a function of the soil surface area available for adsorption, and of the soil natural organic matter, which also adsorbs to, as well as provides adsorptive surface.

Figure 4 presents the compaction test report showing the moisture versus density relationship for the soil, and the maximum compaction of approximately 1.89 g/cm^3 (118 lb/ft^3) at 11 percent moisture content. The compaction test followed the modified Proctor method. Permeability vs density data are presented in Figure 5.

To determine the effect of the degree of soil compaction on the percolation rates through the soil columns being tested, the soil was packed as received, with a natural moisture content of 11 percent. By compacting the soil in the columns to a density of 1.68 g/cm^3 (105 lb/ft^3), a percolation rate of 1.5×10^{-3} cm/sec (i.e., discharge rate divided by column area) was obtained under a constant 60 cm head. The soil column percolation rate measurements provide an estimate of the maximum expected flow rate under laboratory or field conditions. At greater soil densities, the percolation rate (which is proportional to permeability at a given hydraulic head and depth of soil) would be correspondingly lower.

To determine the mineralogical composition of the Freehold soil, X-ray diffraction studies were undertaken by Technology of Materials Company. The sample was prepared by grinding and sieving an aliquot of soil to 200 mesh particle size. This powder was then run in a Phillips Electronics X-ray diffractometer, equipped with a crystal monochrometer. The X-ray diffraction charts were analyzed and phase identifications were made by comparison with standard diffraction data files. The results showed quartz and feldspar to be the only measurable constituents. Quartz was the major phase, representing at least 98 percent of the total weight. No measurable amounts of any clay minerals appeared in the native sample or in a subsample of just the clay sized particles. The color of the Freehold soil suggested iron carbonate or a hydrated iron oxide; however, this color is evidently due to an amorphous iron oxy-hydroxide or hydroxide as no measurable peaks were found representing the suspected phases.

The cation exchange capacity (CEC) of the soil was also determined by Laucks Testing Laboratories, Inc. The total exchangeable metallic cations, and the exchangeable hydrogen were each determined, and the results were added to yield the total CEC. The result was 8.6 milliequivalents per 100 gms, an extremely low value, confirming the absence of mineralogic clay in the soil. The absence of mineral clay and the low CEC could be expected to allow removal of polar organic contaminants from the soil more easily than from a more clayey soil.

The total organic carbon content (TOC) of the soil, as measured by Laucks Testing Laboratories, Inc., (using a Dohrmann DC 80 TOC Analyzer) was 0.12 percent by weight. This relatively low level of organic matter in the soil

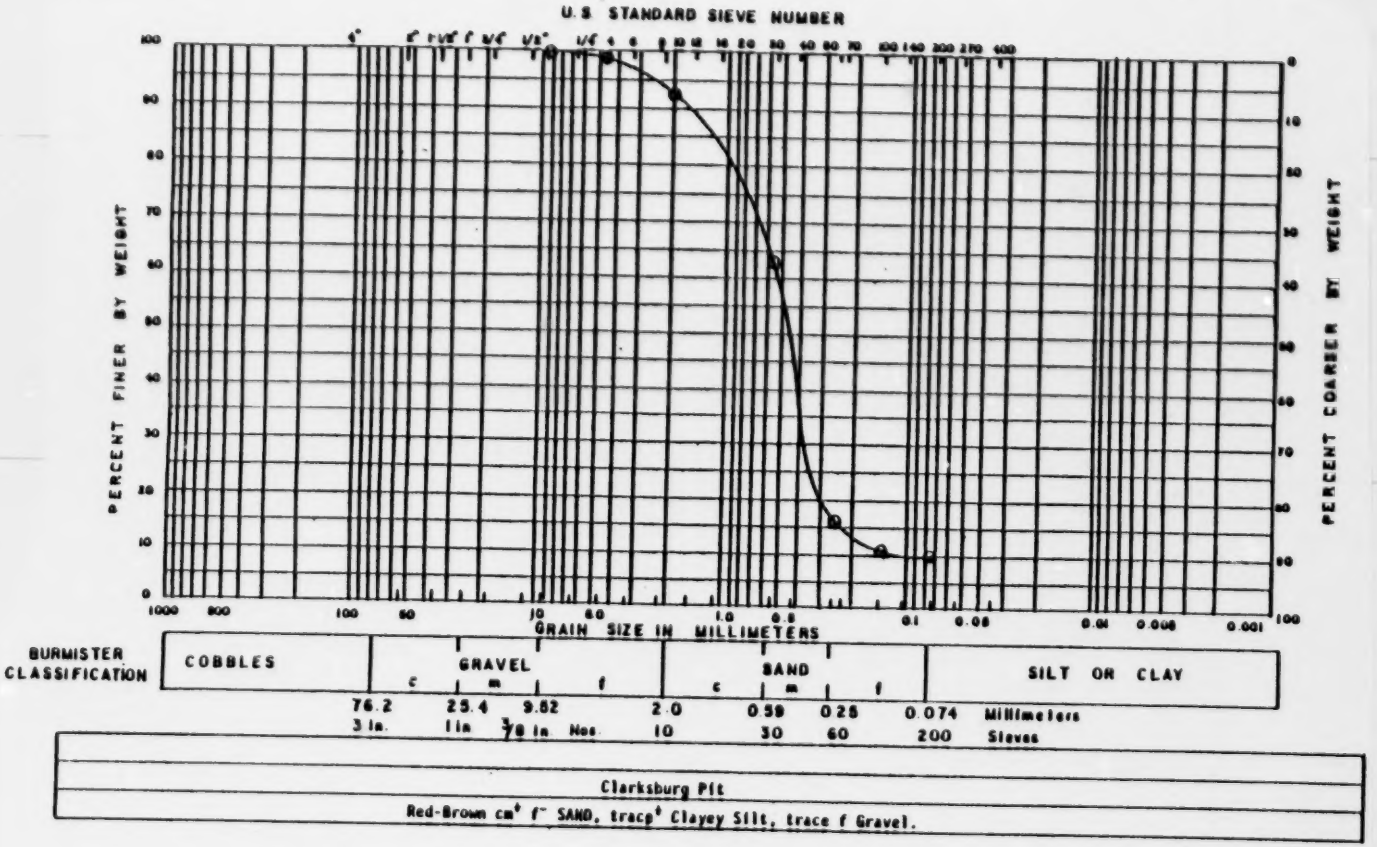

FIGURE 4. COMPACTION TEST RESULTS:
MOISTURE VS. DENSITY RELATIONSHIP

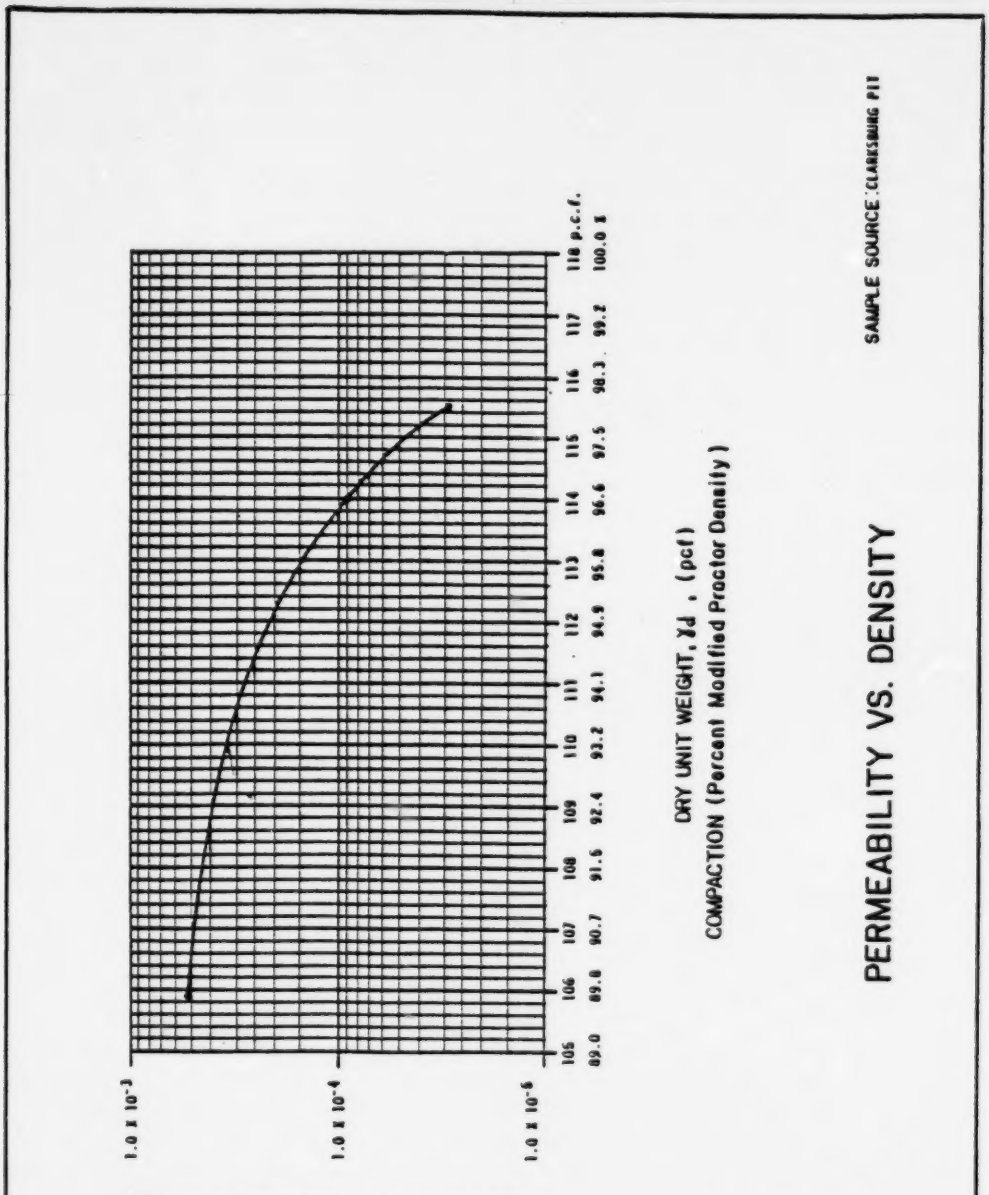
PERMEABILITY VS. DENSITY
SAMPLE SOURCE: CLARKSBURG PIT
COMPACTION (Percent Modified Proctor Density)
DRY UNIT WEIGHT, γd , (pcf)
105 106 107 108 109 110 111 112 113 114 115 116 117 118 p.c.f.
89.0 89.8 90.7 91.5 92.4 93.2 94.1 94.9 95.8 96.6 97.5 98.3 99.2 100.0 %
COEFFICIENT OF PERMEABILITY (cm/sec)
1.0 x 10⁻³
1.0 x 10⁻⁴
1.0 x 10⁻⁵

FIGURE 5. PERMEABILITY VS. DENSITY RELATIONSHIP

implied that the soil would have a relatively low adsorption capacity for organic contaminants. Therefore, contaminants could be expected to wash off relatively easily, compared to a high TOC soil, e.g., 2-4 percent.

6.2 SURFACTANT SELECTION

The results of the water solubility tests of several surfactants and surfactant combinations are presented in Table 10.

TABLE 10. SURFACTANT SOLUBILITIES IN WATER

SURFACTANTS	SOLUBILITY RESULTS
1% Richonate® YLA	insoluble
4% Adsee® 799	soluble
2% Adsee® 799 + 2% Richonate® YLA	soluble
2% Adsee® 799 + 2% Hyonic® NP-90	soluble
3% PFC - 2639	soluble
0.5% ETG[a]	insoluble
0.5% ETG + 1% Adsee® 799	insoluble
0.5% ETG + 1% Hyonic® NP-90	insoluble
0.5% EPG[b]	insoluble
0.5% EPG + 1% Adsee® 799	insoluble
0.5% EPG + 1% Hyonic® NP-90	insoluble
1.5% Active 8000	soluble
1.5% Nepco® 1186-A	insoluble

[a] Emulsan Technical Grade from Petroferm
[b] Emulsan Purified Grade from Petroferm
Manufacturers: Witco Chemical -- Adsee® 799, Richonate® YLA
Diamond Shamrock -- Hyonic® NP-90, Nepco® 1186-A
Petroferm -- PFC-2639, Emulsan
Bullen Chemical Co./Midwest -- Active 8000

Richonate® YLA was not soluble in deionized water to the extent of 1 percent unless mixed with another surfactant (Adsee® 799). A 4 percent combination of Adsee® 799 and Hyonic® NP-90 was soluble. The Petroferm Emulsans, which are lipoheteropolysaccharide biopolymers produced by fermentation, were insoluble even at 0.5 percent (weight/volume), even with 1 percent Adsee® 799 or 1 percent Hyonic® NP-90 added.

The clay and oil dispersion test results, presented in Table 11, showed excellent oil dispersion and minimal clay dispersion by a combination of equal parts of Hyonic® NP-90 and Adsee® 799, which are both nonionic surfactants used as wetting agents. Hyonic® NP-90 is a polyethoxylated nonyl phenol, with an average of 9 ethoxyl groups in the polyethoxy side chain. Adsee® 799 is a blend of polyethoxylated fatty acid esters. Both of the surfactants have been shown in multiple test systems to be biodegradable.

The solubility, minimal clay dispersion, and excellent oil dispersion characteristics of a 1:1 mixture of Adsee® 799 and Hyonic® NP-90 suggested that this mixture would be effective for organics contaminated soil cleanup, and deserved further testing.

6.3 PRELIMINARY SOIL COLUMN EXPERIMENTS

At the beginning of the study, the effect of soil washing with water, followed by 4.0 percent surfactants (2 percent each of Adsee® 799 and Hyonic® NP 90), and a final water rinse was investigated in soil column experiments using the Murban distillation fraction, PCBs, and di-, tri-, and pentachlorophenol contaminants. Separate samples of freehold soil were spiked with 1,000 ppm Murban distillate cut, 100 ppm PCBs, and 30 ppm chlorinated phenols. In each case, nine columns were treated with a 10 pore volume water wash, then a 10 pore volume 4.0 percent surfactant wash, and then an additional 10 pore volume water rinse. The soil columns were sacrificed serially for soil analysis, one after each 3 to 4 pore volumes (called one pass). Duplicate leachate samples were collected and analyzed for the pollutant group of interest at the time of each column sacrifice.

Results of these column experiments are presented in Figures 6 through 8 which show the relative contaminant concentration in the soil and leachate as a function of the treatment stage. The effect of the various wash steps on Murban contaminated soil is seen in Figure 6. The initial water wash had no effect: less than <0.002 percent of the contaminant was detected in the leachate, even after ten pore volumes. However, upon initiation of surfactant washing, 74.5 percent of the pollutants were removed in the leachate after three pore volumes. Additional pore volumes of surfactant increased the amount of Murban distillate cut removed to 85.9 percent after 10 pore volumes. The pollutant concentration in the soil was reduced to 6.18 percent of the initial spike value after the tenth pore volume of surfactant. The final water rinse showed only minimal effects: after the tenth pore volume of water rinse, the soil still contained about 7.0 percent of the initial spike whereas the total amount of contaminant leached was 88 percent. (Note that since the soil and leachate concentrations are based on several different columns treated in parallel, some variability between results at different stages of each test are unavoidable. This variability caused the apparent increase in soil levels between the second pass (pore volumes 4-7) and third pass (pore volumes 8-10) of the water wash, and again between the last pass of surfactant washing, and the subsequent water rinses.)

TABLE 11. RESULTS OF SURFACTANT CLAY AND OIL DISPERSION TESTS

Surfactant(s)	Extent of Clay Dispersion			Oil Dispersion Ability			
	Clearest	Intermediate	Cloudiest	Excellent	Good	Average	Poor
Deionized Water		X					X
4% Adsee® 799						X	
1% Adsee® 799	X						
1% Adsee® 799 + 1% NP-90	X			X			
1% Richonate® YLA			X			X	
1% Adsee 799 + 1% Richonate® YLA			X			X	
0.25% NP-90 + 0.5% Richonate® YLA			X		X		
3% PFC-2639 + 1% Adsee® 799	X					X	
0.5% EPG (a) + 2% Adsee® 799		X			X		
3% PFC-2639		X					X
3% PFC-2639 + 1% NP-90		X		X			
0.5% ETG (b)			X			X	
0.5% ETG + 2% Adsee® 799			X		X		
0.5% ETG + 2% NP-90			X	X			
0.5% EPG			X			X	
0.5% EPG + 2% NP-90			X	X			
1.5% Active 8000			X	X			
1.5% Nepco 1186-A			X	X			

(a) Emulsan Technical Grade from Petroferm

(b) Emulsan Purified Grade from Petroferm

Manufacturers: Witco Chemical -- Adsee® 799, Richonate® YLA
Diamond Shamrock -- NP-90, Nepco® 1186-A
Petroferm -- PFC-2639, Emulsan
Bullen Chemical Co./Midwest -- Active 8000

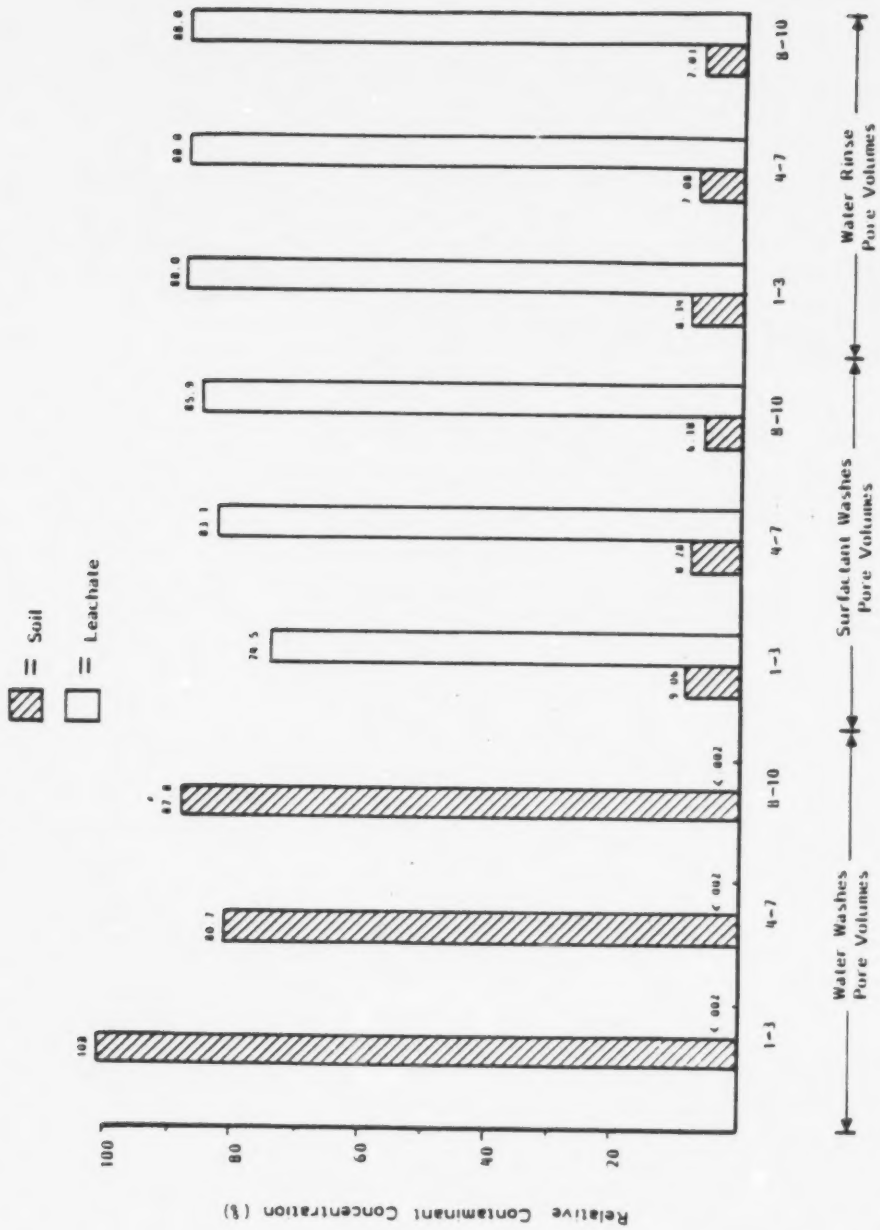

FIGURE 6. MURBAN SOIL COLUMN CLEANUP
WITH 2% OF EACH SURFACTANT

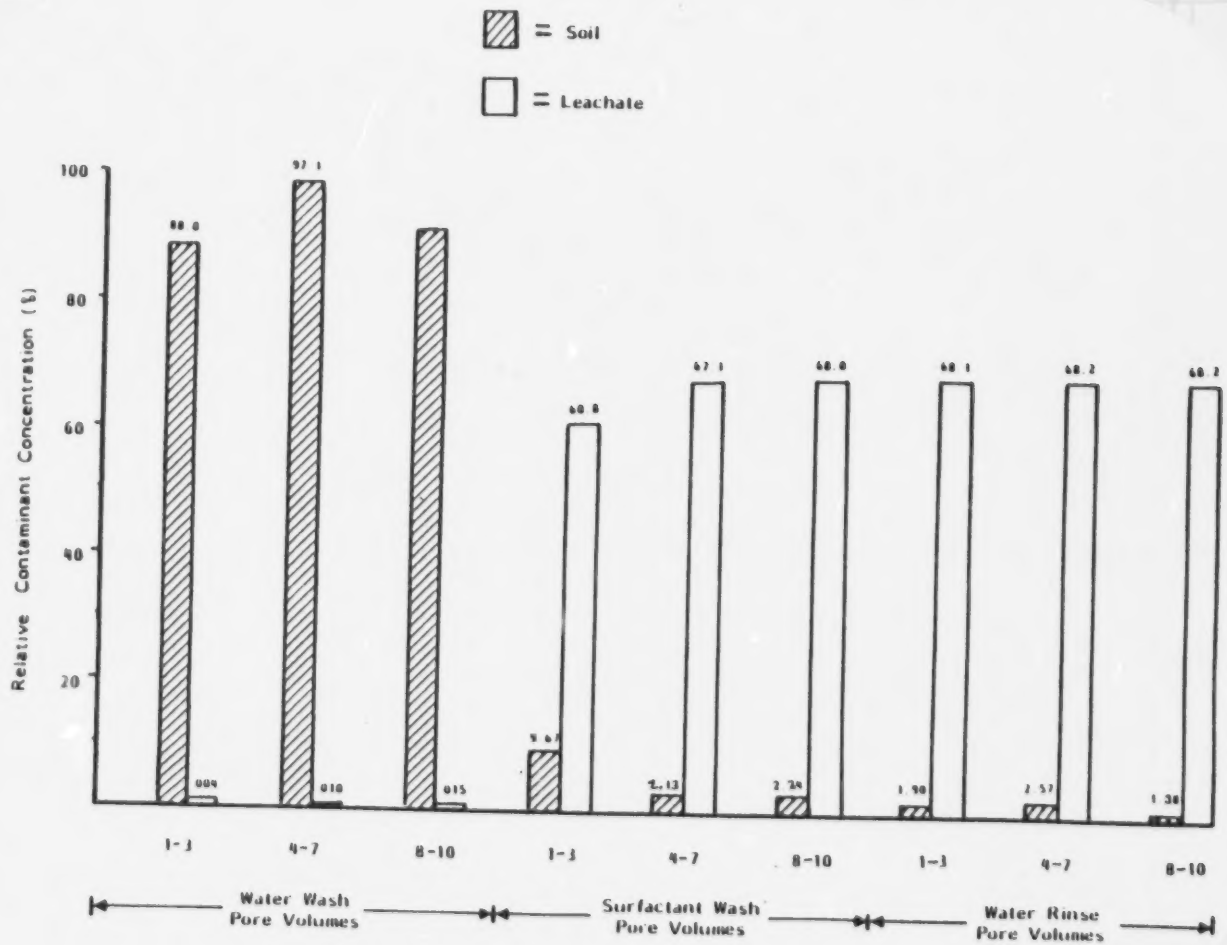

FIGURE 7. PCB SOIL COLUMN CLEANUP
WITH 2% OF EACH SURFACTANT

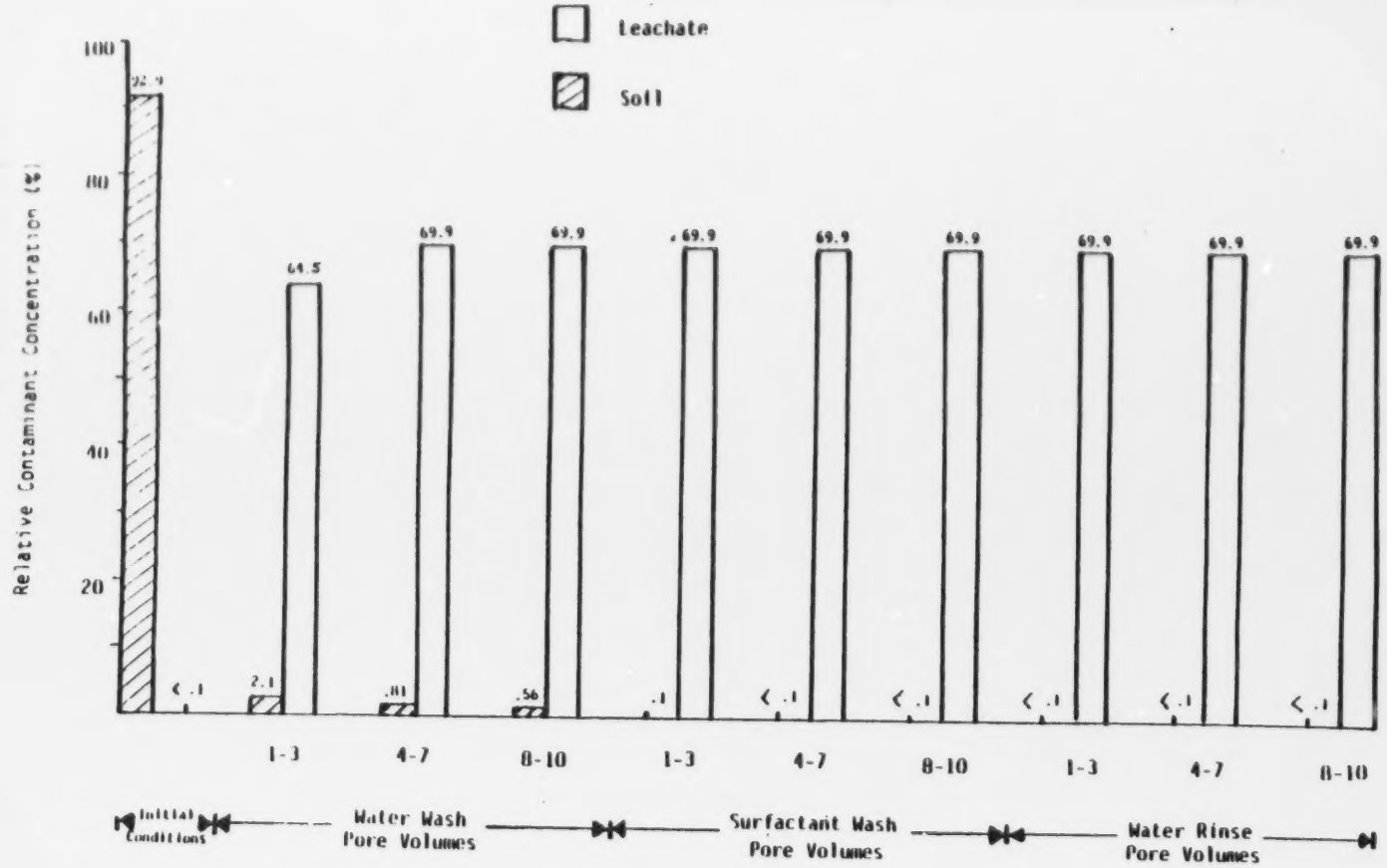

FIGURE 8. CHLORINATED PHENOL SOIL COLUMN CLEANUP WITH 2% OF EACH SURFACTANT

Similar cleanup behavior was observed for the column experiments using PCB spiked soil. Figure 7 shows that the initial water wash was ineffective in cleaning PCBs from the soil with only 0.015 percent being removed after the tenth pore volume. As for the Murban distillate cut column test, the soil was cleaned substantially by the 4.0 percent surfactant solution. In this case, 60.8 percent of the PCBs was detected in the leachate after the third pore volume with less than 10 percent remaining on the soil. After the final tenth pore volume of water rinse, 68.2 percent of the PCBs was detected in the leachate and only 1.38 percent was detectable on the soil.

Similar soil column experiments were also conducted using a 30 ppm chlorophenols mixture and, in contrast to the PCB and Murban results, the bulk of these contaminants was removed with the initial pass of water wash. Figure 8 shows that 64.5 percent of the chlorinated phenols was removed by the first water wash, while only 2.1 percent was detected in the soil. After the third pore volume of surfactant wash, no chlorinated phenols could be detected in the soil while almost 70 percent was found in the aqueous leachate. The surfactant probably interfered with the extraction of the PCBs and chlorinated phenols when the leachate samples were extracted with methylene chloride. Thus, a complete mass balance was not obtained in these early tests, and the leachate plus soil values equal less than 100 percent.

For all contaminant groups investigated, soil washing methods were good, as 68-88 percent of each contaminant mixture was ultimately removed from the soil. The encouraging results obtained from these initial soil column studies warranted further investigations into the feasibility of aqueous surfactant soil washing. The same experimental design was used for further evaluations to optimize surfactant concentrations and leachate treatments (as discussed in the following sections).

6.4 OPTIMIZATION OF SURFACTANT CONCENTRATION

To optimize the cost-effectiveness of a soil washing countermeasure, it was necessary to determine the minimum concentration of surfactant that would yield acceptable soil cleanup. Surfactant concentrations were varied from 0 to 1.0 percent of each individual surfactant in shaker table experiments using both PCB and Murban contaminated soils. Then column experiments were undertaken to verify the shaker table test data and also to narrow the range of viable surfactant concentrations.

6.4.1 Shaker Table Tests

Using Freehold soil with a PCB spike of 100 ppm, a series of surfactant concentrations was examined for soil cleaning potential. One hundred grams of PCB spiked soil was agitated with 200 ml of surfactant solution for one hour, then centrifuged, and the soil and leachate were analyzed for PCB content. The surfactant concentrations tested in duplicate were: 0, 0.001, 0.01, 0.10, 0.25, 0.50, 0.75, and 1.0 percent of each of the two individual surfactants in combination (0 to 2.0 percent total surfactant).

Figure 9 shows the effect of varying surfactant concentrations on PCB partitioning between soil and leachate. There was essentially no cleanup of the soil with surfactant concentrations of 0.25 percent (0.50 percent total) or below. At a concentration of 0.50 percent there were noticeable amounts of PCBs contained in the leachate; cleanup was further enhanced by increasing the surfactant concentration to 0.75 percent. However, increasing the surfactant concentration to 1.0 percent did not further improve cleanup: similar PCB partitioning was observed for 0.75 percent and 1.0 percent surfactant concentrations.

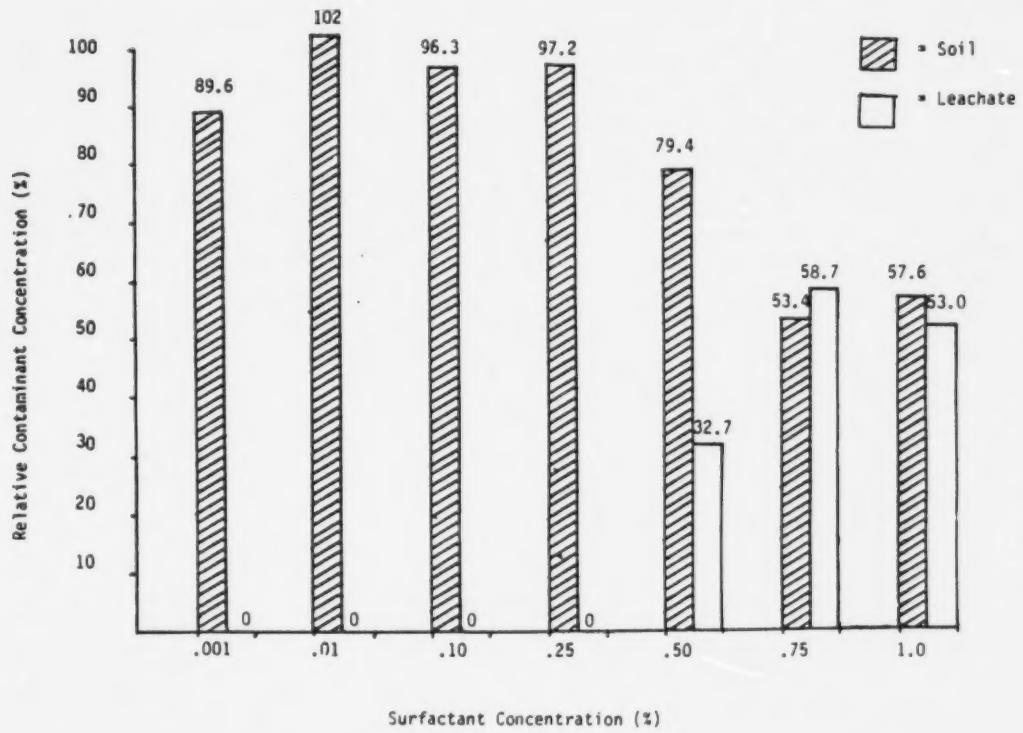

FIGURE 9. PCB SHAKER TABLE
RECOVERIES VS. SURFACTANT CONCENTRATION

A similar shaker table experiment was conducted in duplicate, using the Murban hydrocarbon pollutant at a spike level of 1,000 ppm. The same surfactant concentrations were tested to determine if the optimum concentration was contaminant dependent. Figure 10 presents the relative hydrocarbon content in the leachate and soil for the various surfactant concentrations. Small but measurable amounts of hydrocarbons--ranging from 1.48 to 2.49 ppm--were detected in the leachate with surfactant concentrations of 0.001 percent to 0.25 percent. As with the PCB shaker table experiment, there was enhanced cleanup beginning at 0.50 percent surfactant concentration, with 35.8 ppm hydrocarbons detected in the leachate. Increasing the surfactant concentration to 0.75 percent further enhanced cleanup, with 47.6 ppm hydrocarbon content in the leachate.

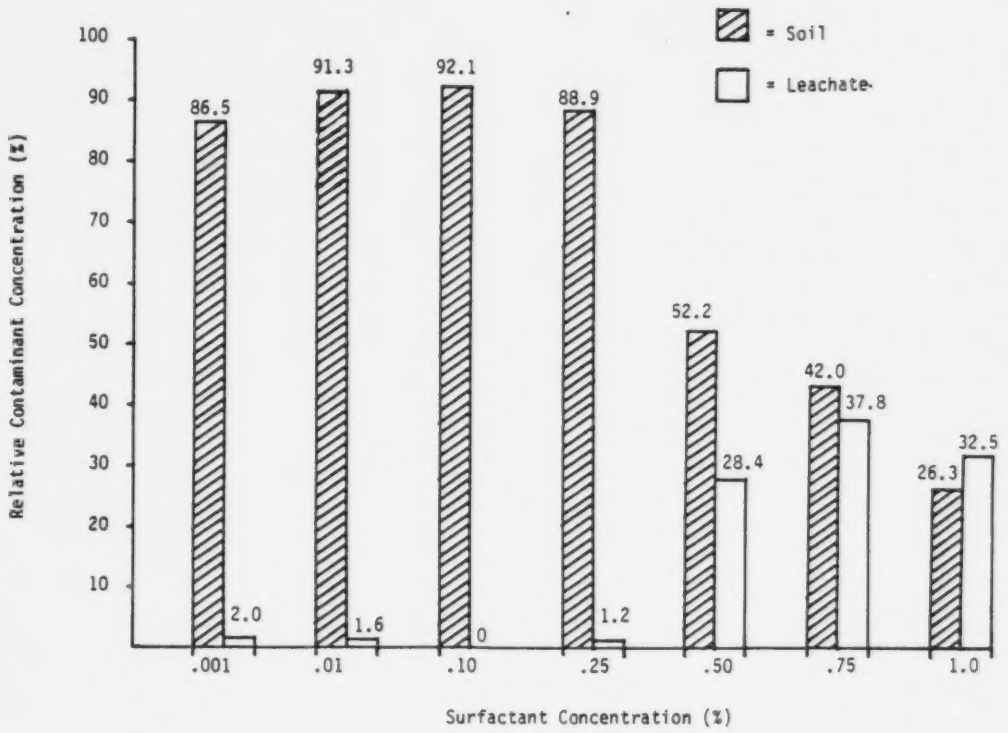

FIGURE 10. MURBAN SHAKER TABLE RECOVERIES VS. SURFACTANT CONCENTRATION

Figures 9 and 10 show that the partitioning behavior (i.e., distribution between surfactant solution and the soil) for hydrocarbons and PCBs with varying surfactant concentrations is somewhat similar. Individual surfactant concentrations of 0.25 percent and below were ineffective; increased surfactant concentrations caused increased soil cleanup from 0.50 percent to 0.75 percent surfactant; however, above 0.75 percent of each surfactant there was little significant enhancement of soil cleanup.

6.4.2 Column Tests

To ensure that the optimum surfactant concentration under gravity flow conditions was not significantly different from the optimum under equilibrium conditions, column tests with various surfactant concentrations were run on soil spiked with 100 ppm PCBs.

Columns were treated with one pass of 0.50, 0.75, and 1.0 percent of each surfactant (1.0, 1.5, and 2.0 percent total surfactant), and the migration and mobilization of PCBs within the column was noted. Columns 1, 2, and 3 received one, two, and three pore volumes, respectively, of 0.50 percent surfactant before sacrifice and soil analysis. Columns 4, 5, and 6 received one, two, and three pore volumes, respectively, of 0.75 percent surfactant before sacrifice. Likewise, columns 7, 8, and 9 received one, two, and three pore volumes, respectively, of 1.0 percent surfactant before sacrifice. Three columns of unspiked soil were used as controls, each one receiving three pore volumes of 0.5 percent, 0.75 percent, or 1.0 percent of each test surfactant.

No initial water washes or final water rinses were run through the columns. The downward migration of PCBs is apparent from the graphical presentation of data in Figure 11, which presents the PCB concentrations in the various portions of the columns as a function of pore volume for each of the three surfactant concentrations tested. A comparison of PCB migration rates indicates that PCB mobilization was greatest at 1.0 percent surfactant, somewhat less at the 0.75 percent surfactant concentration, and much less at 0.50 percent surfactant. This fact can be observed most readily by noting the differences between bottom soil PCB concentrations with the varying surfactants. After the three pore volumes there was a PCB concentration at the bottom of the column of 244 ug/g with the 0.50 percent surfactant, compared to 405 ug/g when using 0.75 percent surfactant and 562 ug/g when using the 1.0 percent surfactant. As Figure 11 indicates, there was a smaller improvement in the PCB migration rates between 0.75 percent and 1.0 percent surfactant concentrations than between 0.50 percent and 1.00 percent.

6.5 EVALUATION OF LEACHATE TREATMENT TECHNIQUES

Large amounts of surfactants and wash water are required for field application of this countermeasure technology. Surfactants are expensive, and for this technology to be cost-effective, surfactant recycling is an important consideration. Accordingly, various leachate treatment techniques were evaluated for their ability to remove and concentrate the contaminants while leaving the surfactants behind for further use. All treatment methods evaluated were ineffective in accomplishing this. It appears that the same

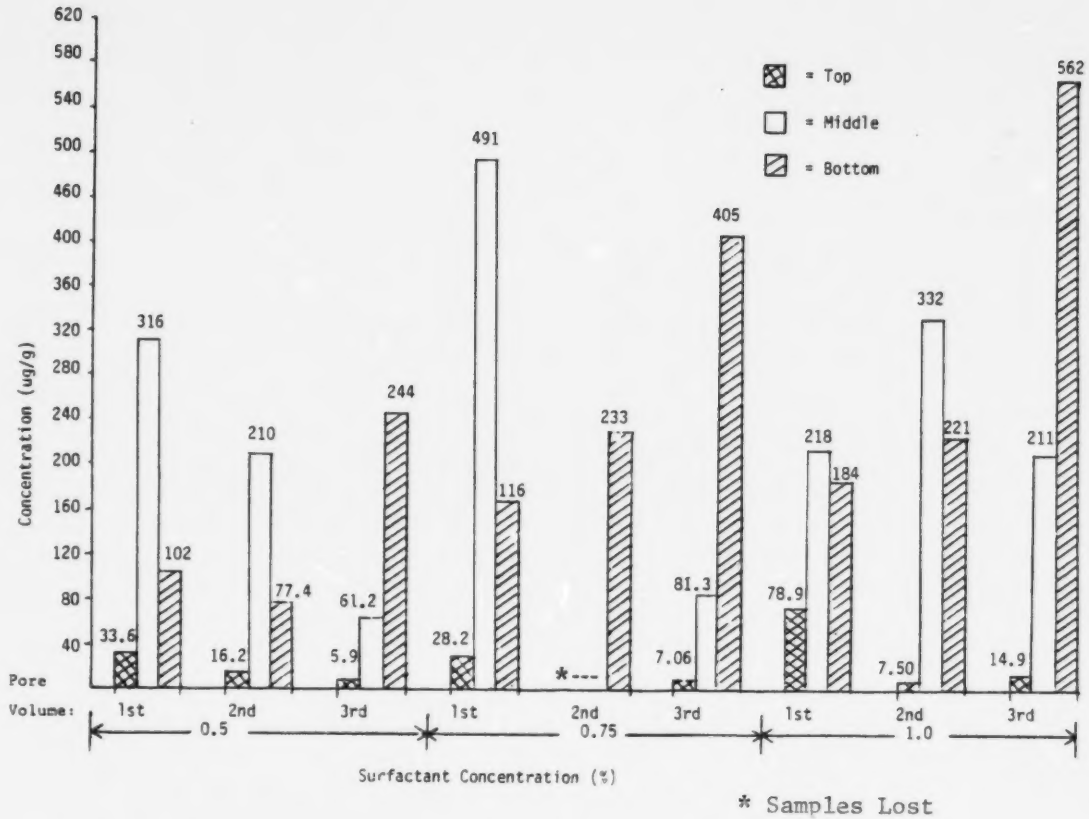

FIGURE 11. PCB SOIL COLUMN CLEANUP
VS. SURFACTANT CONCENTRATION

chemical and physical properties of the surfactant mixture used that act so well to extract the pollutants from the soil also inhibit separation of the contaminants from the surfactants.

As a second consideration, large volumes of contaminated leachate are generated by cleaning soil with aqueous surfactants. Consequently, various leachate treatment techniques were evaluated for their ability to (1) concentrate the contaminants to facilitate disposal, and (2) clean the water enough that it could be sent to a POTW or reused.

Experiments with various leachate treatment alternatives showed that dilute alkaline hydrolysis of a surfactant in the leachate, followed by neutralization, produced a clean aqueous effluent containing a fraction of a percent of salts -- the surfactant components separated from the leachate solution and sank, taking the contaminants with them. Either activated carbon or foam fractionation could be used to further purify the leachate following hydrolysis, producing a very clean effluent. The experiments leading to these results will be described in this subsection.

Evaluation of leachate treatment alternatives for the aqueous surfactant countermeasure has included three phases:

- o Examining potentially feasible leachate treatment methods
- o Preliminary testing of the most feasible methods
- o Adapting the best of the feasible methods for use with soil column tests.

Seven techniques for leachate treatment were identified for initial examination of potentially feasible alternatives:

- o Foam fractionation
- o Sorbent adsorption
- o Ultrafiltration
- o Surfactant hydrolysis/Phase separation
- o Flocculation/Coagulation/Sedimentation
- o Centrifugation
- o Solvent extraction.

Foam fractionation, sorbent adsorption, and ultrafiltration, were considered most likely to be feasible techniques for leachate treatment, so they were subjected to preliminary laboratory tests using simulated leachate. Surfactant hydrolysis was also tested; the idea was conceived by SAIC staff as a novel method for leachate cleanup. The goal in leachate treatment was to remove the contaminants from the leachate solution, and isolate them in a concentrated form. Partial or complete recycle of the surfactants, because of their high cost in field scale applications, was also a goal. This was not, however, attained with any of the treatment methods.

The other three techniques initially considered, flocculation/coagulation/sedimentation, centrifugation, and solvent extraction, were considered to be much less feasible, for reasons explained in Section 6.5.2, Less Feasible Treatment Alternatives.

6.5.1 Laboratory Tests of the Most Feasible Treatment Alternatives

Preliminary laboratory tests of foam fractionation, sorbent adsorption, hydrolysis, and ultrafiltration were conducted to assess the feasibility of these methods for removing the contaminants from leachate following surfactant washing of soils. All of these methods were effective for removal of contaminants in the preliminary tests, described below. Ultrafiltration was the

only method not further developed through tests with actual column leachate; time and budget limitations precluded further work. The only treatment method that effectively removed contaminants from the raw leachate was hydrolysis, which destroyed one of the surfactants in the leachate and made it impractical to recycle the other.

6.5.1.1 Foam Fractionation

Foam fractionation is one of several separation methods which involves the selective adsorption of surface-active solutes (surfactants) at the gas-liquid interfaces of bubbles rising through a liquid column. As gas is bubbled through a solution containing a surfactant, a surfactant-rich foam forms at the top of the column. Removal of the foam as it forms results in a gradual reduction of surfactant concentration in the liquid column, and simultaneous removal of any liquid or solid contaminants suspended in the liquid.

Foam separation techniques are ideally suited to removing the surfactants and associated contaminants from the collected leachate. The removal efficiency of the technique is mostly dependent on three variables:

- o Bubble size
- o Gas flow rates
- o Surfactant concentration.

The experimental system to test foam fractionation techniques was initially a single fractionation column using a batch process. The column design is depicted in Figure 12. Diffusers which produced a range of bubble sizes were employed, because in most of the published studies reviewed, bubble size was not tightly controlled.

The results of the batch foam fractionation tests, presented in Table 12, show that good clean up of the leachate was achieved if the concentration of surfactant was below about 0.1 percent, while no significant reduction in surfactant occurred if the starting concentration was above that.

For example, in Run #3, the surfactant concentration in the model leachate was decreased from a starting concentration of 0.013 percent to only 0.003 percent in the final residue, a decrease of 77 percent. The volume of the starting leachate decreased by only 13 percent (from 485 ml to 420 ml in the residue), the balance becoming foamate, the liquid which condenses from the surfactant-laden foam. The net effect, 77 percent of the surfactant becoming concentrated in only 13 percent of the liquid volume reflects a substantial reduction in volume of leachate. This could be improved through further foam fractionation steps. However, starting with surfactant levels of 0.045 percent (Run #5), the foamate contained 87 percent of the surfactant, but was also 54 percent of the liquid volume. At 0.128 percent starting surfactant, using a continuous flow mode of fractionation, the performance was even worse: the level of surfactant after 108 minutes of foam fractionation decreased by only 5 percent (from 0.128 percent to 0.122 percent).

The foam fractionation system was upgraded to a multistep continuous process for testing the cleanup efficiency for leachate solutions using a more

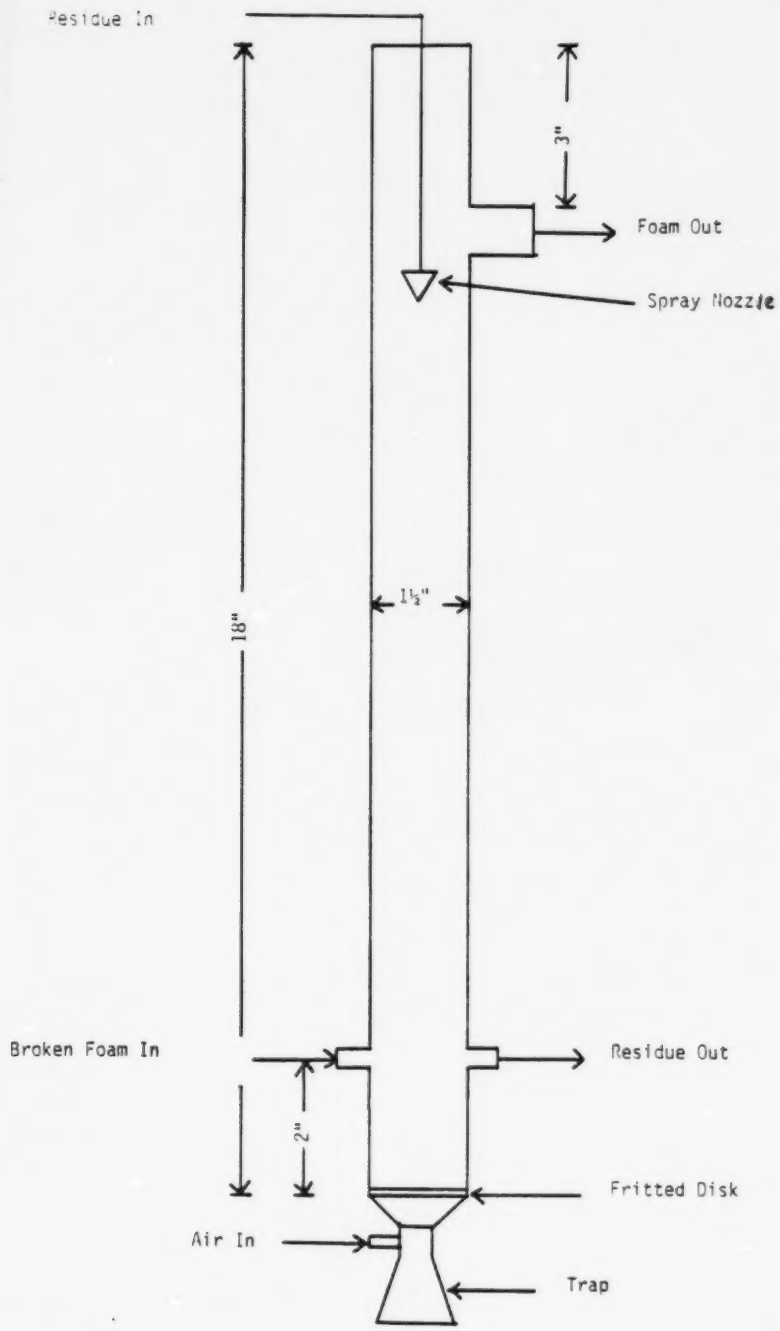

FIGURE 12. BENCH SCALE FOAM FRACTIONATION COLUMN

TABLE 12. SINGLE COLUMN FOAM FRACTIONATION CLEANUP RESULTS

Run #	Sample	Concentration (%)	Volume (ml)
2	Starting Surfactant	.013	500
"	Time Final Residue	.003	310
"	Foamate	.064	-[a]
3	Starting Surfactant	.013	485
"	Time Final Residue	.003	420
"	Foamate	.064	-
4	Starting Surfactant	.032	480
"	Time Final Residue	.003	335
"	Foamate	.041	-
5	Starting Surfactant	.045	490
"	Time Final Residue	.006	225
"	Foamate	.056	-
7	Starting Surfactant	.390	360
"	Time Final Residue	.336	255
"	Foamate	.678	-
8	Starting Surfactant	.133	360
"	Residue #1	.134	-
"	Time Final Residue	.133	-
"	Foamate	.144	-
9	Starting Surfactant	.128	Continuous Flow
"	Residue @ 42 min.	.124	"
"	Foamate @ 42 min.	.134	"
"	Residue @ 61.5 min.	.110	"
"	Foamate @ 61.5 min.	.126	"
"	Residue @ 83.3 min.	.119	"
"	Foamate @ 83.3 min.	.132	"
"	Residue @ 108 min.	.122	"
"	Foamate @ 108 min.	.312	"

a - Foamate volumes can be calculated by difference, continuous flow volumes can be obtained by rates

efficient design. Dual column, multiple pass foam fractionation was tested for treating 1.5 percent surfactant solutions with and without 2.0 percent calcium chloride (added to promote phase separation following hydrolysis). The results were consistent with the results of the batch foam fractionation tests. The high concentration of surfactant found in the raw column leachate could not be reduced using foam fractionation, even with an ionic species added to the solution to promote separation. The foamates showed no increase in surfactant concentration over the residue. Even if the leachate removed through extraction wells in field tests of the surfactant countermeasure would be diluted two- to threefold by groundwater, this leachate would still be too concentrated for treatment by foam fractionation.

Foam fractionation was further tested for polishing low surfactant level solutions after preliminary treatment by other methods. (See Subsection 6.5.1.3, Surfactant Hydrolysis and Phase Separation.)

6.5.1.2 Sorbent Adsorption

Eleven solid sorbents were screened to determine their efficiency in removing PCBs and the surfactants from an aqueous solution. The sorbents were tested by adding one gram of each sorbent to 50 ml of model leachate containing 1.5 percent total surfactant and 1.10 mg of PCB, swirling for 5 minutes and letting stand for 10 minutes. The sorbents tested and their performance in this experiment are summarized in Table 13. None of the sorbents was very efficient in removing PCBs from a surfactant solution. A removal efficiency of about 1g per gram of sorbent represents good sorption efficiency.

The most efficient sorbent for PCB removal was the Filtrol XJ-8401, with an efficiency of 0.00045 g/g, followed by WV-B 14x35, WV-G 12x40, and WV-L 8x30 Activated Carbons, and Celkate magnesium silicate. The surfactants are apparently as effective in removing PCBs from, or preventing their adsorption to, sorbent materials as in removing PCBs from soil.

For selective removal of PCBs from solution in preference to the surfactant, the WV-B 14x35 Activated Carbon was best, with 19 percent PCB removal compared with 11 percent removal of the surfactants. Thus, even though the overall adsorption efficiency of the sorbents in the presence of surfactants is low, small amounts of very hydrophobic compounds could be removed if a sufficiently large proportion of sorbent were used. For relatively toxic materials like PCBs, this may be practical.

6.5.1.3 Surfactant Hydrolysis and Phase Separation

Hydrolysis treatment of the surfactant and contaminant containing leachate was tested to find if the Adsee® 799, a fatty acid ester, would form a separate organic phase upon hydrolysis which contained both the surfactants and the organic contaminants. The first tests of hydrolysis for leachate treatment involved boiling the solution with approximately one equivalent of acid for 0.5 hr, followed by neutralization with a base, addition of salt, and cooling to allow separation of the organic phase. Salt was also added to the hydrolysis mixture to promote separation of the organic

TABLE 13. SORBENT BATCH TEST RESULTS

Sorbent Name	Removal Efficiency[a] (grams adsorbed/grams sorbent) PCB	Surfactant
Filtrol Grade XJ-8308 (clay pellets)	.00011	.150
Filtrol Grade XJ-8401 (clay pellets)	.00045	(b)
QS-13683 (clay pellets)	.0002	.180
Airfloated Bond Filter (clay pellets)	.00016	.090
Sorbo Cel (Celite diatomite)	.00021	.090
Celkate (magnesium silicate)	.00028	.195
WVB-14x35 (granular activated carbon)	.00032	.083
WVG-12x40 (granular activated carbon)	.00028	.195
WVL-8x30 (granular activated carbon)	.00028	.150
WVW-12x40 (granular activated carbon)	.0002	.105
Oil Loc (expanded basalt)	0.0	.120
Control (no sorbent)	0.0	0.0

a - One gram of each sorbent was added to 50 ml of leachate containing 1.5% surfactant and 1.10 mg of PCB, swirled for 5 minutes, then let stand for 10 minutes.

b - Sample lost

phase from the aqueous phase. The reuse of the aqueous salt solution from treatment of the contaminated leachate for treatment of another sample of contaminated soil, by dissolving additional fresh surfactants, was tested in a shaker table experiment. Because of the high (8 percent) content of salt in the water solution following hydrolysis, the PCB removal with the recycled solution was only 34 percent as efficient as removal with new surfactant solution. The salt content was mainly the calcium chloride which was added to the leachate solution to promote phase separation following hydrolysis (see Table 14); acid neutralization also produced a salt.

In later tests of hydrolysis treatment, hydrolysis with a strong base such as sodium hydroxide was found to promote better separation of the organic phase than acid-catalyzed hydrolysis, so alkaline conditions were used for all subsequent hydrolyses.

Although foam fractionation and sorbent adsorption could be used as polishing methods for removing traces of contaminant and surfactant from leachate solutions, only hydrolysis with a strong base was found to be an effective initial treatment for the higher surfactant concentrations found in the raw leachate. To reduce the volume of aqueous salt solution generated by leachate treatment, thereby allowing the water to be recycled and minimizing the cost of disposal during field implementation, treatment procedure modifications were tested.

TABLE 14. BASE HYDROLYSIS TREATMENT OF LEACHATE

Sample #	Description	Concentration (mg/l)		Volume (ml)	Total Mass (mg)	
		PCB's	Surfactant		PCB's	Surfactant
PCH-1	Starting Leachate	19.8	15,000	250	4.95	3750
PCH-2	Aqueous Phase After Hydrolysis (w/$CaCl_2$)	.137	24	330	0.0452	7.9
PCH-3	Oil Phase After Hydrolysis (w/$CaCl_2$)	205	(a)	16.3	3.34	-
PCH-4	Aqueous Phase After Hydrolysis (no $CaCl_2$)	2.10	–	234	0.491	-
PCH-5	Oil Phase After Hydrolysis (no $CaCl_2$)	155	–	59.0	9.15[b]	-

a - Not analyzed
b - Suspect non-homogeneous sample

A synthetic PCB leachate was treated by hydrolysis without adding salt; only the 0.1 percent of salt from base neutralization was left in the solution. Alkaline hydrolysis of 6 l of this leachate, containing 16 ppm of PCBs in 1.44 percent aqueous surfactants, followed by neutralization, yielded 6.9 l of treated aqueous solution with only 0.017 percent of surfactants remaining; a small (0.09 l) separate layer of surfactant hydrolysis products containing 95.4 percent of the PCBs (1100 ppm PCBs) also formed.

Further treatment of the aqueous surfactant solution with a column of activated carbon (WVB 14x35) yielded a solution containing only 0.01 ppm of PCBs.

Following hydrolysis, the treatment of the aqueous effluent by foam fractionation was also shown to remove the residual surfactants from the leachate. A four-column series of foam fractionation columns operating in a continuous countercurrent flow mode was used (see Figure 13). The test results demonstrating this are summarized in Table 15. Both the final salt level (1800 ppm) and the residual PCB level (0.0036 ppm) should be low enough to allow disposal to a publicly owned treatment works, and were low enough to permit reuse of the leachate water for soil cleaning.

The cleanup of a soil column spiked with PCBs, by recycling the treated leachate water for successive passes of aqueous surfactants through the column, was as effective as with fresh surfactant solution (see Section 6.6, Evaluation of Leachate Recycling). The recycled leachate was treated by alkaline hydrolysis/phase separation, with polishing by granular activated carbon. The final PCB level in the treated leachate was only 0.57 ppb.

6.5.1.4 Ultrafiltration

Ultrafiltration is a hydraulically driven separation technique that employs a thin (0.1 - 0.5 micron) semipermeable membrane integrally bonded to a highly porous polymeric substrate for filtering very fine particles from a suspension under pressure. The Millipore Pellicon Cassette system, which was used for testing, utilizes a transverse-flow geometry to continually sweep the membrane clear. For our tests we used a 460 cm^2 (0.5 ft^2) Millipore PT series membrane with a pore size equivalent to a molecular weight cutoff of 10,000. The PT series membrane consists of polysulfone on a polyethylene support.

Testing was conducted on two leachate types; the first consisted of approximately two liters of an aqueous phase after hydrolysis, containing 0.546 percent surfactant, to which was added 20 mls of saturated polyvinyl alcohol (PVA) in water. PVA is a safe, inexpensive, water-soluble polymer, with an average molecular weight of 40,000. The addition of PVA was thought to be a way to promote a polymer-surfactant complex that would stabilize large surfactant micelles, thus allowing efficient filtration. The second test was conducted on straight 3.3 percent (total) surfactants without any complexing agent. Test results are presented in Table 16.

The first 100 ml of filtrate was discarded, then an aliquot was collected and its surfactant concentration was determined to be 0.0026 percent. A

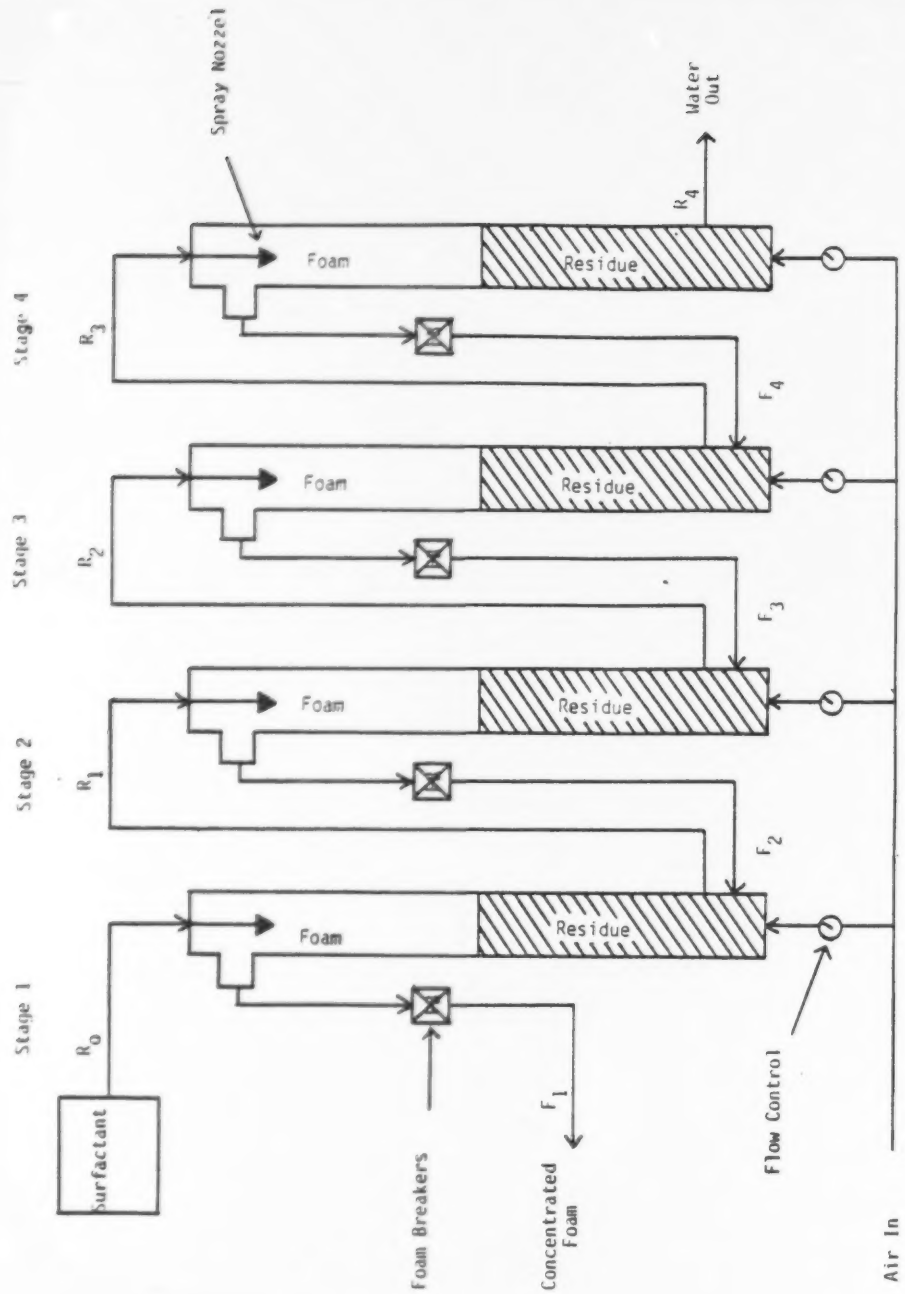

FIGURE 13. COUNTERCURRENT FOAM FRACTIONATION SCHEME

composite and, therefore, more representative sample was obtained after 540 ml of filtrate had been collected and it showed a concentration of 0.025 percent while the remaining retentate had concentrated to 0.696 percent.

The system was allowed to flush with DI water before the second test was conducted. After discarding the first 100 ml of filtrate, 150 ml of filtrate was collected. The filtrate sample was analyzed and its surfactant concentration was 0.27 percent, while the retentate had concentrated to 3.79 percent.

It should be noted that time did not allow for running the tests to completion, which might have resulted in a tenfold reduction in the retentate volume. The results presented here represent approximately 40 minutes of filtering time per test.

TABLE 15. HYDROLYSIS AND FOAM FRACTIONATION TREATMENT OF LEACHATE

	PCB's	Surfactant	Salt	Volume
Starting Simulated Leachate	105 mg	110 g	0 g	8000 ml
Aqueous Phase After Hydrolysis	0.47 mg	2.47 g	8.2 g	6970 ml
Oil Phase After Hydrolysis	142 mg	n.a.*	n.a.*	120 ml
Concentration Changes in a Treated Aliquot				
Starting Simulated Leachate	13.1 ppm	13,800. ppm	0 ppm	6190 ml
Aqueous Phase After Hydrolysis	0.067 ppm	354. ppm	1200 ppm	5390 ml
Oil Phase After Hydrolysis	1180. ppm	n.a.*	n.a.*	92.7 ml
Aqueous Phase After Foam Fractionation	0.0036 ppm	209. ppm	n.a.*	5030 ml
Foamate Phase	0.100 ppm	1280 ppm	n.a.*	360 ml

*not analyzed

6.5.2 Less Feasible Treatment Alternatives

Three techniques initially considered feasible for leachate treatment were not tested in the laboratory because other methods seemed more promising for efficient cleanup, and because of budget limitations for the project. The reasons for considering these techniques less feasible than the ones tested are presented in the next three subsections.

TABLE 16. ULTRAFILTRATION TEST RESULTS

Test #	Sample	Volume (ml)	Concentration (%)
1	Initial leachate before PVA	1950	0.546
1	Initial leachate with PVA added	1960	0.531
1	First filtrate	----	0.0026
1	Composite filtrate	540	0.025
1	Retentate	1420	0.696
2	Initial leachate	1350	3.30
2	First filtrate	----	0.144
2	Composite filtrate	150	0.270
2	Retentate	1200	3.79

6.5.2.1 Flocculation/Coagulation/Sedimentation

The addition of materials to the leachate solution to encourage the formation of settleable flocs appears to have little potential for leachate cleanup. The formation of flocs requires that the suspended material to be removed have a surface charge, which results mainly from the presence of ions, leading to coagulation of the suspended particles in the presence of appropriate polyvalent ionic flocculation materials.

Removal of suspended solids from the leachate, especially soil particles, occurs as it moves through the soil column and as it exits the column through a glass wool filter. Fines are also removed through settling in the leachate

receiving vessel. However, removal of the very fine surfactant-contaminant droplets (micelles) requires more stringent methods. The micelles will not have full ionic charges at their surface, and the charges at their surface due to polarization and electron delocalization within the surfactant molecules are not likely to be strong enough to produce efficient floccing. Sweep floccing, in which very large amounts of flocculant literally sweep the particles out of suspension was considered possibly feasible, but not practical.

6.5.2.2 Centrifugation

The settling of contaminant-surfactant particles suspended in the leachate solution might be accelerated by centrifugation if the particles were denser than the solution. In the case of PCB cleanup, this would occur; but in the more general case in which the bulk of the contamination is hydrocarbons, the suspended particles will probably be less dense than the aqueous solution. Centrifugation would not be very effective in that case.

6.5.2.3 Solvent Extraction

Solvent extraction of the organic contaminants from the aqueous leachate appeared infeasible because whenever solvent extractions of the solution were performed in the laboratory during work-up for analysis, inseparable emulsions formed. These emulsions broke very slowly, preventing phase separations for hours. Furthermore, the extraction of low concentrations of organics from an aqueous solution using an organic solvent can be expected to contaminate the solution with the extraction solvent at a level significantly higher than the level of the organic contaminants being removed.

6.6 EVALUATION OF LEACHATE RECYCLING

6.6.1 Column Tests With Untreated Leachate

To evaluate the effect of recycling the aqueous leachate on soil cleanup a PCB soil column experiment was conducted. Eight columns were packed, as before, with Freehold soil spiked with 100 ppm PCB. Two control columns were packed identically, but with no PCB spike.

For comparison purposes, four columns received one, two, three, and four passes (three, six, nine, or twelve pore volumes) (three pore volumes equals one pass) of fresh 0.75 percent surfactant before being sacrificed, while four other columns received similar amounts of recycled untreated surfactant solution before sacrifice. Recycling of raw leachate was accomplished by reintroducing it to the top of the column. Three pore volumes of surfactant solution (6 l) was used four times.

The data from the raw leachate recycling column experiment are presented graphically in Figures 14 and 15. Figure 14 compares the soil PCB concentrations in the fresh surfactant solution and the recycled (raw) leachates. Figure 14A shows that fresh surfactant solution cleaned the top third of the column first, and then the middle, followed by the bottom. In Figure 14B, the effect of recycling leachate on the top portion of the column is shown. It never gets as clean as when using fresh surfactant, and actual concentrations increase from 5.71 ug/g PCB after the third pass to 34.1 ug/g PCB after the fourth pass. Also, Figure 15 shows that after the third pass with fresh surfactant, a "plug" of PCBs (182 mg) eluted off the column. This never occurred with recycling--probably because of repartitioning of the PCBs onto the previously cleaned top fraction of soil. Good cleanup of all portions of the column was achieved after four passes of fresh surfactant; however, recycling treatment at the same stage showed only limited cleanup at best. Figure 15 presents a comparison of the total relative PCB concentration in the whole soil versus the leachate for both fresh and recycled surfactant. Only 6.9 percent of the PCBs remained on the soil after four passes of fresh surfactant, while 43.4 percent of the PCBs remained on the soil after four passes with leachate recycling.

6.6.2 Column Tests With Treated Leachate

Because recycling untreated leachate proved to be unacceptable, a column experiment was devised in which the recycled leachate received treatment between each pass. Four PCB spiked columns and one unspiked control column were packed as before.

Four passes of surfactant solution were put through the columns, with leachate recycling after each pass. The aqueous leachate was treated by hydrolysis, followed by adsorption by activated carbon, remade back up to 1.5 percent total surfactant and allowed to pass through the column again. The leachate was analyzed for PCB content before hydrolysis, after hydrolysis, and after activated carbon treatment. The oil phase, which is the product of hydrolysis, was also analyzed for PCB content. After each pass one of the columns was sacrificed and the top, middle, and bottom sections were also analyzed for PCBs.

The result of leachate hydrolysis was a relatively small volume of a waxy, oil phase. Because of their hydrophobic nature, the contaminants present in the leachate tended to preferentially partition out of the aqueous leachate and into this oil phase. In other words, the aqueous surfactant solution passed through the contaminated soil column and extracted the contaminants, resulting in a large volume of uniformly contaminated surfactant mixture. Upon hydrolysis, the surfactants separated out as an oil phase and carried the contaminants with them. This resulted in a relatively clean volume of water and a highly contaminated, much smaller volume of waxy oil phase.

After hydrolysis, the oil and water phases were separated and the water was further treated by passage through columns of activated carbon. Chromatograms of extracts of leachate after secondary treatment with activated

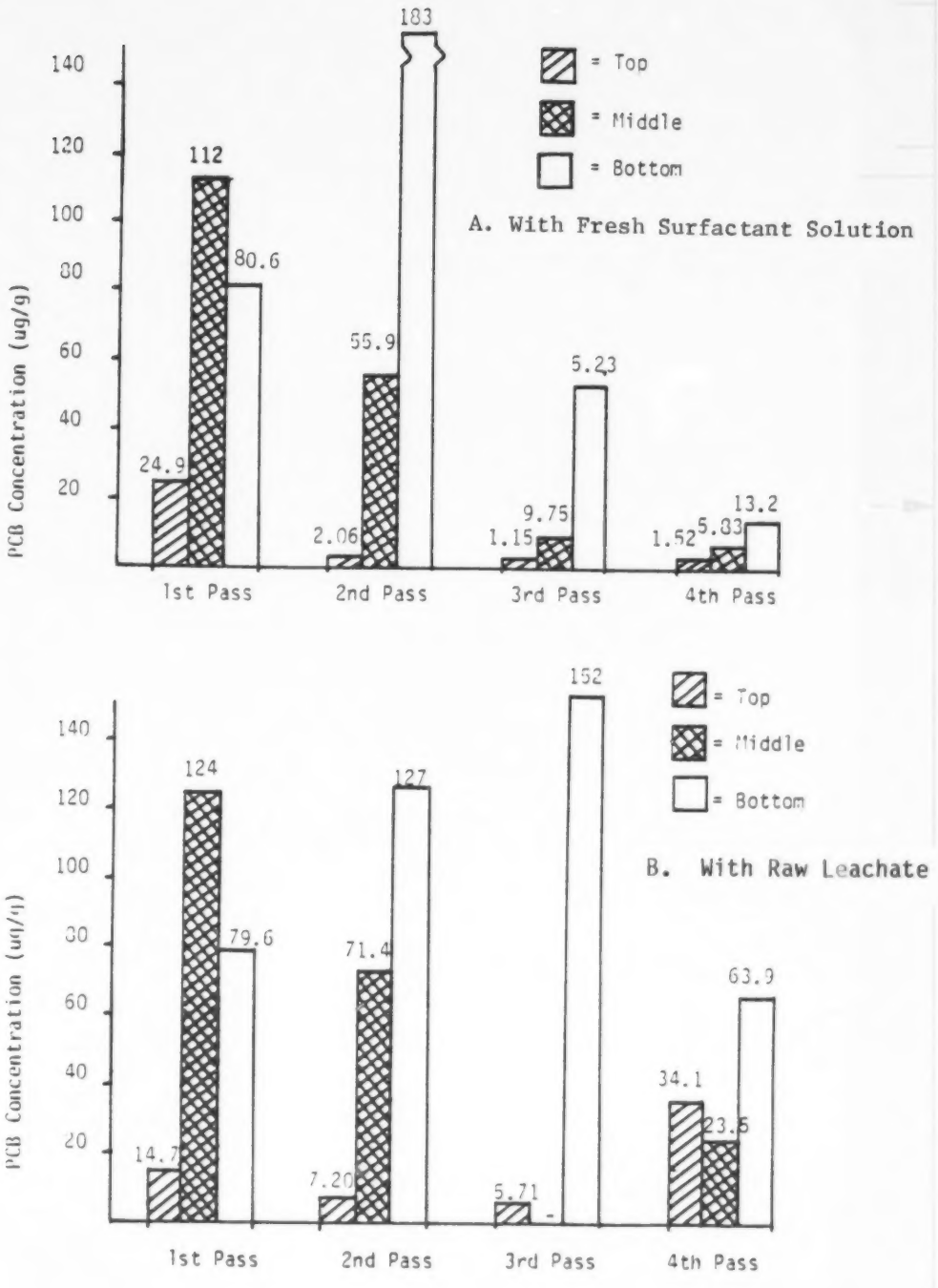

FIGURE 14. RAW LEACHATE RECYCLING:
PCB COLUMN SOIL LEVELS

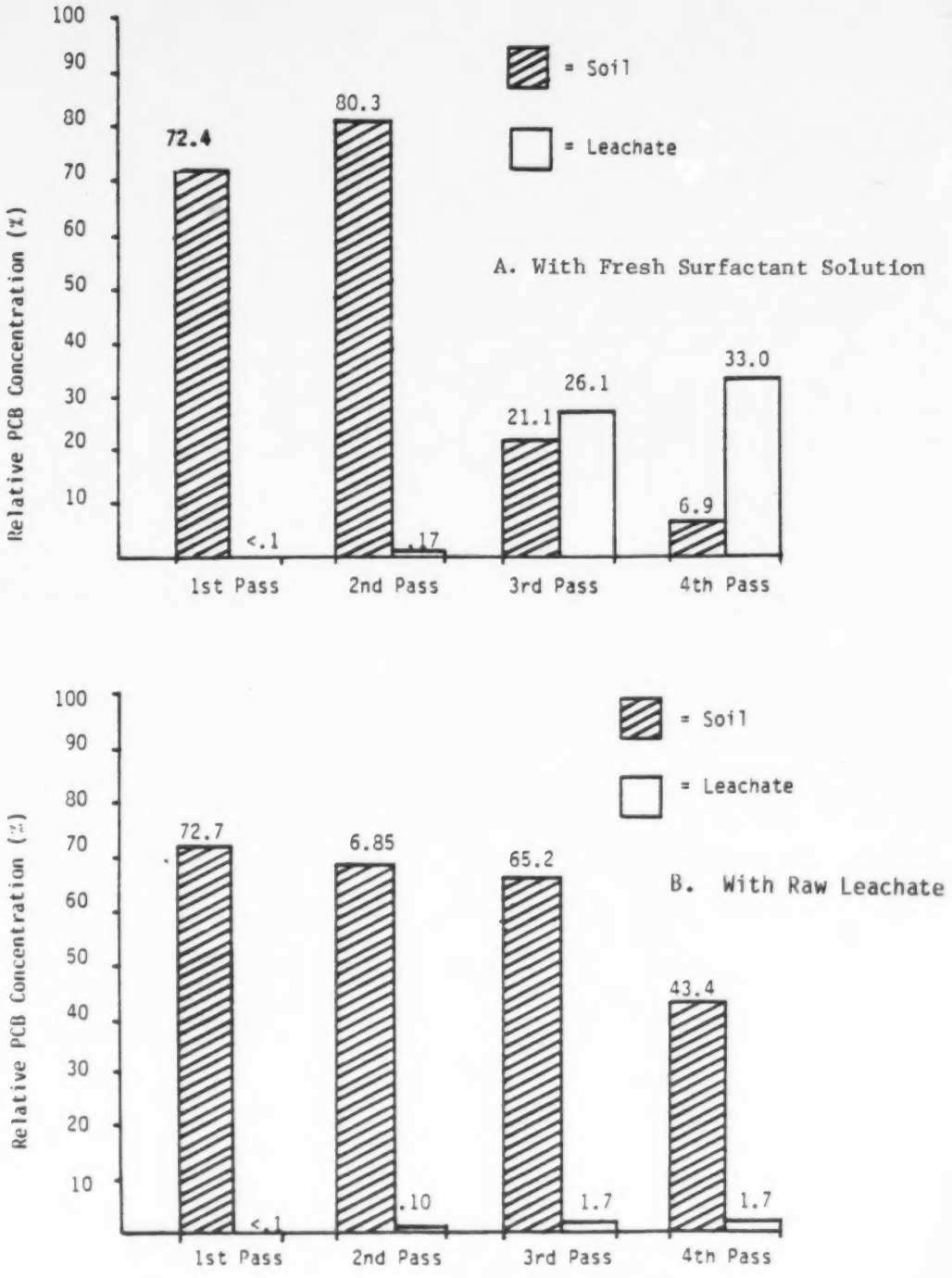

FIGURE 15. RAW LEACHATE RECYCLING:
SOIL AND LEACHATE RESULTS

carbon showed detectable amounts of PCBs even after the third pass; however, after the fourth and final pass there were no PCBs present in the leachate.

After leachate treatment, the surfactant concentration was measured and, in most cases, found to be less than 0.01 percent. Therefore, between each pass fresh surfactant was added to the treated leachate prior to recycling, and the soil in the column received four passes of fresh surfactant. Only the water was recycled.

Soil cleanup was successful. Figure 16 shows the PCB concentration for the top, middle, and bottom portions of the column. The PCBs tended to accumulate toward the bottom of the column before elution from the column. After the fourth pass, only 6.17 mg of PCBs remained on the column (down from an initial spike of 697.5 mg per column). This represents less than one percent of the original soil contamination. Figure 17 shows the partitioning behavior of PCB between soil and leachate as a function of the number of passes delivered.

TABLE 17. PCB LEVELS IN HYDROLYSIS AND SORBENT TREATED LEACHATE

	PCB Content (total mg)			
	First Pass	Second Pass	Third Pass	Fourth Pass
Before Hydrolysis	653 ± 113	106 ± 3.0	16.8 ± .8	6.32
After Hydrolysis	1.21 ± .57	.448 ± .306	.539 ± .221	.0839
After Activated Carbon	.115 ± .021	.0697 ± .0423	.0488 ± .0173	.00285
Cumulative mg removed from soil	653	759	776	782
Cumulative %[a] removed from soil	93.6	108.8	111.3	112.1

[a] - based on an initial spike of 697.5 mg/column

Results of duplicate leachate analysis are presented in Table 17, which shows how effective the treatment method was. After the first pass, the leachate contained 653 mg of PCB before treatment. After hydrolysis, the PCB content was reduced to 1.21 mg and, following secondary treatment (by activated carbon), the PCB concentration was further reduced to 0.115 mg. As the soil

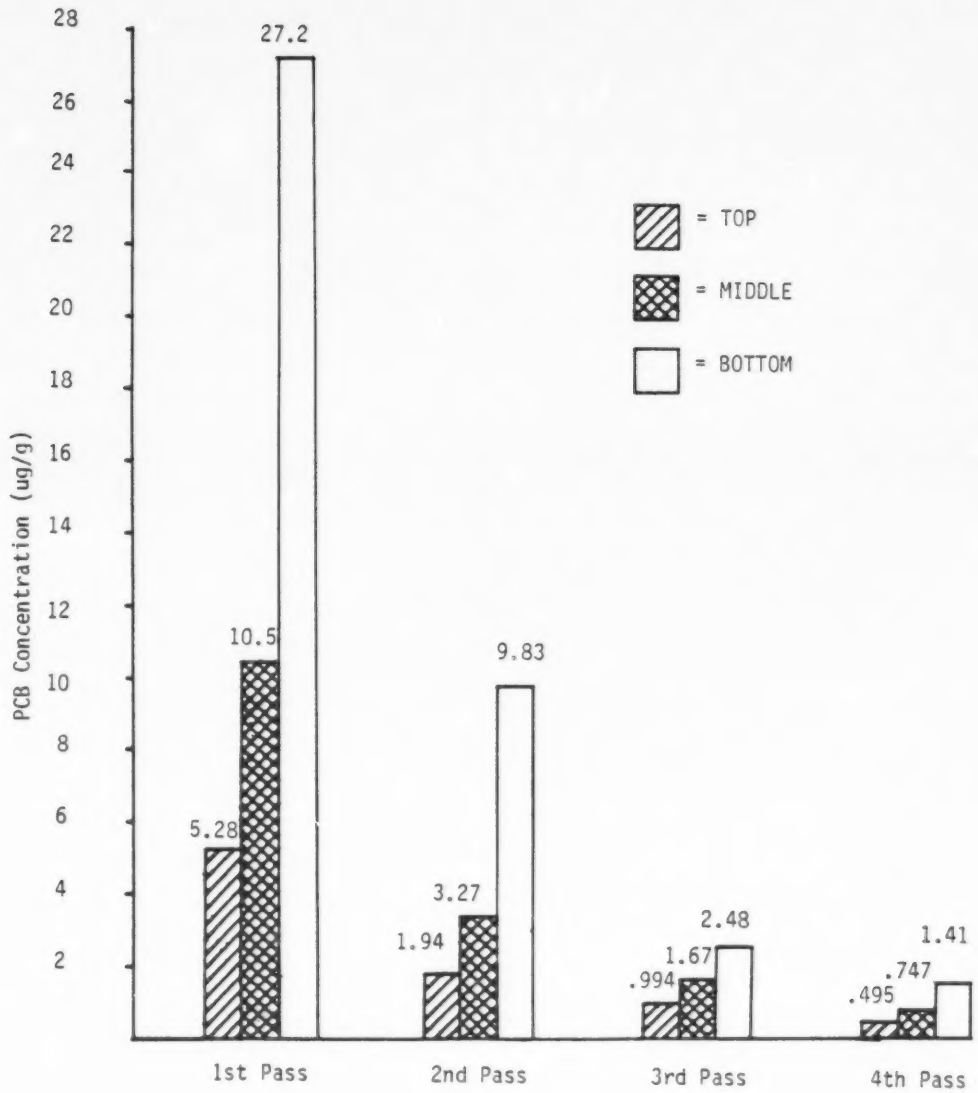

FIGURE 16. TREATED LEACHATE RECYCLING:
PCB COLUMN SOIL LEVELS

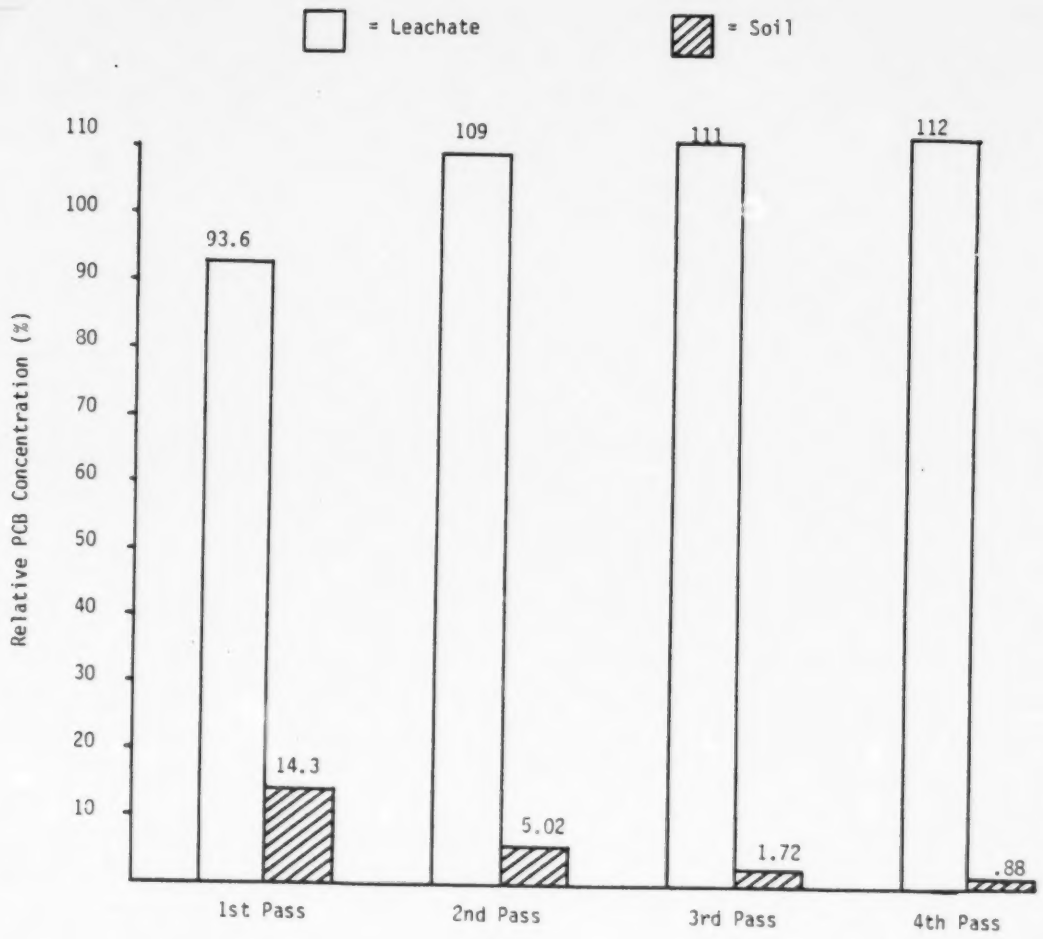

FIGURE 17. TREATED LEACHATE RECYCLING:
SOIL AND LEACHATE LEVELS

column was cleaned of PCBs with each pass, the contaminant concentration in the leachate was also reduced, as shown in the table. With reduced PCB content in the leachate, treatment became more effective, as indicated by the PCB content in the leachate after the fourth pass. After the fourth pass, only 6.32 mg was present in the untreated leachate; primary treatment removed all but 0.0839 mg and this value was reduced to 0.00285 mg by treatment with activated carbon. Used repeatedly, and initially contaminated with up to 131 ppm (653 mg/5.0 l) PCB, the contamination in the leachate was ultimately reduced to 0.00057 ppm (0.00285 mg/5.0 l), of PCBs.

The ultimate fate and mass balance of the PCB contamination is summarized in Table 18, where the PCB mass and volume or weight of the matrix is delineated for the initial conditions, each pass, and the final conditions. The initial conditions show that 697.5 mg PCB are contained in 6,975 grams of soil, which is the 100 ppm soil spike. The final conditions show that only 6.17 mg of PCBs remained on the 6,975 grams of soil, only 0.00285 mg was present in the 5.03 l of treated water, while 641 mg of the PCBs was contained in only 609 grams of oil phase material.

TABLE 18. PCB MASS BALANCE FOR HYDROLYSIS AND SORBENT TREATED LEACHATE

	Oil Phase	Soil Phase	Treated Water Phase
INITIAL CONDITIONS		697.5mg in 6,975g	
First Pass	512mg in 114g	99.9mg in 6,975g	.115 mg in 4.70 ℓ
Second Pass	82.4mg in 118g	35.0mg in 6,975g	.0697mg in 4.93 ℓ
Third Pass	39.8mg in 200g	12.0mg in 6,975g	.0488mg in 5.71 ℓ
Fourth Pass	6.50mg in 145g	6.17mg in 6,975g	.00285mg in 5.03ℓ
FINAL CONDITIONS	641mg in 609g	6.17mg in 6,975g	.00285mg in 5.03ℓ

Mass Balance: 641 + 6.17 + 2.28* .00285 = 649.5mg 93.1%

* Sum of PCB mg before activated carbon

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APPENDIX A

SHAKER TABLE EXTRACTION PROCEDURE

- A 150-200 gram aliquot of soil was transferred to a clean, tared Teflon jar and the sample weight was accurately determined
- A 25-50 gram aliquot of soil was transferred to a tared aluminum cup and placed in a 105C oven for dry weight analysis
- The soil sample was initially extracted with 200 ml of methanol for a 2-hour drying period
- The jar was centrifuged at 2500 RPM for 15 minutes and the methanol extract removed and set aside for future use
- 200 ml of 35:65 methanol/methylene chloride solution was then added to the extraction vessel and the sample was agitated for a 12-hour period
- The jar was centrifuged at 2500 RPM for 15 minutes and the methylene chloride extract was removed; all three filtered extracts were transferred to a separatory funnel
- 500 ml of 3% sodium chloride organic-free water was added to the separatory funnel, and the organics were repartitioned by shaking the separatory funnel
- At this point, the phases were separated by draining the methylene chloride phase through a sodium sulfate drying column (25 grams) into a Kuderna-Danish (K-D) flask
- The methanol/water phase was extracted 3 times with 50 ml of methylene chloride and the combined methylene chloride extracts were passed through the sodium sulfate drying column, into the K-D flask; another 300 ml of methylene chloride was then passed through the drying column.

APPENDIX B

GAS CHROMATOGRAPHY RUN CONDITIONS AND RUN PROGRAMS

Conditions for Gas Chromatographic Analysis:

Column: SE54-30N 30 meter fused silica capillary

Column pressure: 10 to 15 psi using He as the capillary inlet carrier gas (flow rate 1.5 ml/min)

Injection: 1 ul splitless, using auto-injection sampler

Split vent: 30-40 ml/min

Septum purge: 1-1.5 ml/min

ECD makeup gas: argon/10% methane @ 30-40 ml/min

FID makeup gas: hydrogen @ 30-40 ml/min; air at 260 ml/min; nitrogen at 30-40 ml/min.

Integration parameters: zero @ 20% full scale deflection; slope sensitivity @ 0.30; integrator area reject @ 1,000,000,000 area counts

Run Program for a Murban Distillation Fraction:

Time (minutes)	Action
0	Oven temperature at 45C
0.75	Inlet purge (backflush) begins
3	Integrator Area Reject reset to 100 area counts (i.e., solvent peak has eluted)
5	Oven temperature assumes rate of 3.5C/minute

Time (minutes)	Action
72	Oven temperature reaches 280C and stabilizes
80	Stop run

Retention times: Hexamethylbenzene (internal standard) elutes at 28 min, n-decylcyclohexane (internal standard) elutes at 36 min.

Run Program for a PCB Extract:

Time (minutes)	Action
0	Oven temperature at 50C
0.75	Inlet purge (backflush) begins
3	Integrator area reject reset to 100 area counts (i.e., solvent peak has eluted)
3	Oven assumes a rate of 5C/minute
25	Oven assumes a rate of 2C/minute
75	Oven attains a temperature of 250C and the run is terminated.

Retention Times: Lindane (internal standard) elutes at 37 minutes. The Arochlor 1260 mixture elutes between 41 and 66 minutes.

APPENDIX C

HIGH PERFORMANCE LIQUID CHROMATOGRAPHY
RUN CONDITIONS AND RUN PROGRAMS

Preparing for HPLC Analysis:

Column: Bondapak C18, 30 cm long with 10 um diameter packing.

Solvents: A - 1% Aqueous Acetic Acid
B - Acetonitrile

Injection Volume: 100 ul

Flow: 2 ml/min

Oven Temperature: 30C

Recorder settings: chart speed @ 0.50 cm/min;
zero @ 20%;
slope sensitivity @ 0.10;
integrator area reject @ 1,000,000,000 area counts

Run Program for Chlorinated Phenols:

Time (minutes)	Action
0	90% solvent A, 10% solvent B
2.0	A solvent gradient of +12.5% B/min is initiated
4.0	At 35% B a solvent gradient of +4.2% B/min. is initiated
5.0	Area reject is changed to <100 area counts
10.0	60% B is reached and the solvent gradient is terminated

Time (minutes)	Action
14.0	A solvent gradient of +10% B/min is initiated
18.0	100% B is reached
25.0	A solvent gradient of -15% B/Min is initiated
31.0	10% B is reached and the solvent gradient is terminated
32.0	Stop Run

Retention times: 4-chloro, 3-methylphenol (internal standard) elutes at 8.8 minutes; dichlorophenol at 9.3 minutes; trichlorophenol at 10.5 minutes; and pentachlorophenol at 12.9 minutes.

APPENDIX D

CALCULATIONS AND QUALITY CONTROL FOR
INSTRUMENTAL ANALYSIS

Calibration and Calculations

- Prior to the analysis of sample extracts, the linearity of detection for the internal standards and the compounds of interest was demonstrated. These compounds were analyzed at a minimum of three concentrations over the range of interest and response factors generated for each concentration.

$$RF = \frac{Q_c}{A}$$

where:

RF = response factor in ng of compound per GC or HPLC area count (A)

Qc = quantity of the compound on the GC or HPLC column (concentration of standard in ng/ul x injection volume in ul)

- A calibration graph was prepared where the amount (Q) was plotted against the area count (A). Using this method, the linear range of detection for the internal standards and the compounds of interest was determined and all future sample extracts were analyzed within this range. If a sample was too concentrated or dilute it was reanalyzed at a concentration which was in the linear detector response range.

- During analysis of a real sample the sample weight or volume was determined and a known amount of internal standard in methanol was spiked into the sample.

- Determination of the concentrations of pollutants in a sample was accomplished through the use of the following equation.

$$C = \frac{A_p}{W \text{ (or } V)} \times \frac{Q_{is}}{A_{is}} \times \frac{RF_p}{RF_{is}}$$

where:

C = concentration of the pollutant in the dried soil (ng/g) or aqueous leachate (ng/l)

A_p = integrated area under the peak for the pollutant of interest in the sample extract

RF_p = response factor for the pollutant of interest (as determined by the standard)

Q_{is} = quantity of internal standard (in ng) added to the sample extract

A_{is} = integrated area under the peak for the internal standard in the sample extract

RF_{is} = response factor for the internal standard (as determined by the standard)

W = weight of dry soil analyzed (in grams)

V = volume of aqueous leachate analyzed (in liters)

This equation corrects for the recovery of the internal standards during the extraction and concentration steps. The instrument was calibrated (and new response factors generated) after every 10 injections. This minimized the effect of instrument performance on reported results.